Transport and deposition of colloidal particles in microchannel flow

Harikrishnan Narayanan Unni

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Transport and Deposition of Colloidal Particles in Microchannel Flow

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Dedicated to my parents, my wife and to my sister & family

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ABSTRACT

The emergence of Lab-on-a-Chip technologies has instilled an ever-growing interest in the design and analysis of microfluidic systems. During biochemical analyses involving microfluidic devices, particle deposition (surface fouling) can sometimes cause hindrance to the optical detection of the test particles. Also, when the particles and channels are of comparable size, the boundary effects on particle motion become significant. Even though many previous studies have been devoted to understanding particle deposition from pressure driven flows, limited efforts seem to have appeared in the modeling of transport, interaction and deposition of colloidal particles from electrokinetic flows. Hence, this dissertation is in pursuit to investigate the transport and deposition of colloidal particles from pressure driven and electrokinetic microfluidic flows, both theoretically and experimentally, with the objective of establishing the fundamental understanding of particle behavior in these flows, which could serve as useful input to the design and operation of microfluidic devices.

The work done during this study can be split into three parts. Firstly, a deterministic mathematical model is developed to analyse the particle deposition from pressure driven flow in a parallel plate microchannel. The mass transport equation that incorporates hydrodynamic flow, colloidal and external forces, is solved numerically to obtain the particle deposition rates corresponding to various electrolyte concentrations and Reynolds numbers. An optical videomicroscopic system that employs a predesigned parallel plate flow chamber is set up for *in situ* detailed quantification of particle deposition under various solution concentrations and flow rates. Steady state particle deposition rates obtained from theoretical modeling are

compared with results from videomicroscopic experiments that employ the parallel plate flow technique.

Secondly, theoretical simulations using the Brownian dynamic simulation technique are carried out to model particle deposition from pressure driven and electrokinetic microchannel flows in a parallel plate microchannel. This study is performed with a motive to investigate the kinetics of particle deposition phenomena in pressure driven and electrokinetic flows, in the high surface coverage regime. A stochastic model based on Langevin equation which incorporates the colloidal, hydrodynamic interactions and external forces such as gravity is developed to compute particle surface coverage under various physicochemical conditions. A parallel plate electrokinetic flow cell is designed and fabricated, and videomicroscopic experiments are conducted by varying the particle size, solution concentration and electric field strength. The theoretical results are validated by the results from experiments using the parallel plate flow technique and reasonable agreement is found.

The third part of this thesis is devoted to the analytical modeling of multiparticle electrophoresis in parallel plate microchannels. This study is driven by the lack of information in the existing literature on the boundary effects on multiparticle electrokinetic transport in microchannels. The solutions of Laplace equation governing the electrical potential and Stokes equation for the flow field are formulated analytically. This is performed by an analytical inversion of the Fourier transform of wall disturbances (expressed by Fourier integrals) to satisfy the boundary conditions on the surface of the spheres, where the disturbance due to the spheres are represented by spherical harmonic functions. The analytical results for the case of axisymmetric

motion of a single sphere in a parallel plate microchannel are validated using the existing literature. Also, the off-centre motion of a sphere in a microchannel is investigated, and it is found that the eccentricity of particle motion in a microchannel enhances both the translational and rotational velocity. Furthermore, the planar motion of two spheres in a microchannel is studied using the proposed model. The theoretical results show that, in the bulk fluid, particles with smaller size and larger zeta potential travel faster and can overtake larger particles or particles with lower zeta potential. However, the near wall motion of two spheres shows that the effect of zeta potential is overcome by an increase in electrical potential surrounding the particles, whereas the effect of particle size still remains dominant.

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NOMENCLATURE

a_p	Particle radius (m)
a_1	Radius of interacting particle 1
a_2	Radius of interacting particle 2
A	Hamaker constant for particle-wall Van der Waals interactions
A_j	Hamaker constant for interparticle Van der Waals interactions
A_p	Ratio of particle radius to half channel depth
Ad	Adhesion number
B	Half channel height (m)
C	Electrolyte concentration (M)
D_x	Diffusivity in X direction (m^2 / s)
D_y	Diffusivity coefficient in Y direction (m^2 / s)
D_∞	Stokes-Einstein diffusivity (m^2 / s)
DI	Double layer parameter in the HHF expression for EDL interactions
Da	Double layer asymmetry parameter in the HHF expression for EDL interactions
E_∞	Applied electric field strength (V/m)
$f_1(H)$	UHCC correction function for particle diffusion perpendicular to the channel wall
$f_3(H)$	UHCC correction function for particle diffusion parallel to the channel wall
$f_4(H)$	Correction coefficient for diffusivity in x direction

F_x	X component of the total force acting on the particle (N)
F_y	Y component of the total force acting on the particle (N)
$\overline{F}_{EDL}$	Dimensionless EDL interaction force
$\overline{F}_G$	Dimensionless gravity force (Gravity number)
$\overline{F}_{VDW}$	Dimensionless Van der Waals interaction force
h	Surface to surface particle-wall separation distance (m)
h_j	Surface to surface interparticle separation distance (m)
H	Dimensionless particle-wall separation
H_j	Dimensionless interparticle separation
H_0	Dimensionless Primary energy minimum separation
H_∞	Dimensionless particle separation in the bulk fluid
H_{nn}	Generalized Hankel transform
J_k	Analytical Bessel function of k^{th} order
j_x	X component of mass flux ($1/m^2s$)
j_y	Y component of mass flux ($1/m^2s$)
$\overline{j}_x$	Dimensionless mass flux in X direction
$\overline{j}_y$	Dimensionless mass flux in Y direction
K_n	Modified Bessel function of the second kind
k_B	Boltzmann's constant (J/K)
L	Length of the microchannel (m)
n	Particle number concentration (m^{-3})

$\bar{n}$	Dimensionless particle number concentration
n_∞	Bulk particle number concentration (m^{-3})
Pe	Peclet number based on mean flow velocity
P_n^k	Associated Legendre polynomial having order n and degree k
Re	Reynolds number based on mean flow velocity
r_j	Radial coordinate corresponding to the j^{th} sphere in spherical harmonics
Sh	Sherwood number
t	Time (sec)
T	Absolute temperature (K)
U_s	Reference velocity for electrokinetic particle transport (m/s)
u_{eof}	Electroosmotic flow velocity between two parallel plates (m/s)
u_{pdf}	Pressure driven flow velocity between two parallel plates (m/s)
u_{ekp}	Resultant particle velocity in electrokinetic transport (m/s)
V_m	Mean flow velocity in the microchannel (m/s)
V_R	Interaction energy (J)
$\bar{x}$	Dimensionless channel length
z	Ionic valency
e	Fundamental charge, $1.602 \times 10^{-19} J$ (C)

GREEK SYMBOLS

α	Transformed dimensionless particle separation
β	Transformed dimensionless channel length

ϵ_0	Permittivity of vacuum, $8.845 \times 10^{-12} \text{ C}^2 / \text{Nm}^2$
ϵ	Permittivity of fluid medium (C^2 / Nm^2)
ϵ_r	Relative Permittivity
ϕ	Electrical potential in the fluid
φ_j	Azimuthal angle corresponding to the j^{th} sphere in spherical harmonics
Γ	Analytical Gamma function
γ	Particle spacing ratio defined as, $\gamma = 2a_p / (b + c)$
κ	Debye-Huckel parameter defined as, $\kappa = \sqrt{\frac{2z^2 e^2 n_\infty}{\epsilon k T}}$ (1/m)
λ	Retardation wavelength for Van der Walls interactions (m)
$\bar{\lambda}$	Dimensionless retardation wavelength
μ	Dynamic viscosity of liquid (Ns / m^2)
θ	Dimensionless surface coverage
θ_j	polar angle corresponding to the j^{th} sphere in spherical harmonics
ν	Kinematic viscosity of liquid (m^2 / s)
ρ_f	Fluid density (Kg/m^3)
ρ_p	Particle density (Kg/m^3)
τ	Dimensionless adsorption time
ζ_p	Particle zeta potential (mV)
ζ_w	Channel wall zeta potential (mV)
ζ_{p1}	Zeta potential of interacting particle 1 (mV)

ζ_{p1}	Zeta potential of interacting particle 2 (mV)
$\bar{\zeta}_p$	Dimensionless particle zeta potential
$\bar{\zeta}_w$	Dimensionless channel wall zeta potential

CHAPTER 1 INTRODUCTION

1.1 Background and Motivation

The recent advances in the vast expanding field of biomedical science have been achieved through the development of Lab-on-a-Chip microfluidic devices that are employed for various biochemical applications such as drug delivery, electrophoretic or dielectrophoretic separation of bioparticles, detection of bioparticles (e.g. proteins, DNA). These devices have the advantages of low processing time, consumption of low sample volumes, high throughput and portability, that make them preferred candidates for biotechnological applications. These microfluidic circuits can be designed to accommodate virtually any analytic biochemical process and integrate sample input, dilution, reaction, and separation etc. within the same device.

The microfluidic flows can be pressure driven or electrokinetic (driven by an applied electric field) in general, but electrokinetic flows largely find applications in bioanalytic devices due to the advantages such as absence no need of moving parts, simple designs, easy control over sample handling etc. Electrokinetic transport in microchannels involves both the transport of colloidal particles in response to the applied electric field (electrophoresis) and the motion of liquid resulting from the interaction between the electric double layer of the channel and the applied field (electroosmosis). Deposition of the test particles onto the walls of the microfluidic devices can sometimes cause hindrance to the optical detection of these particles. After conducting an extensive review of the available literature on the kinetics of particle transport and deposition, it can be concluded that the present studies on particle transport and deposition focus mostly on

CHAPTER 1

pressure driven flow in microchannels of various geometry. However, as most of the Lab-on-a-chip based microfluidic devices utilize on electrokinetic flows, it would be interesting to explore the particle behavior in electrokinetic flows in relevance to the design and analysis of such systems. Another important issue is the electrical and hydrodynamic particle interactions, which can be of significance in the case of the flow of dense suspensions in a microchannel. Therefore, it would be worthwhile to look into the physics of particle interactions in microchannels and their effect on particle deposition, especially in electrokinetic flow, with an objective to provide useful insight for Lab-on-a-Chip design. In addition, an important point to be stressed here is that, numerous microfluidic devices may involve the transport of particles whose size is comparable to that of the microchannel. Therefore, a thorough understanding of the boundary effects on electrokinetic particle transport becomes important to the design and development of such microfluidic devices. Extensive literatures have been reported on the boundary effects on colloidal particle transport in pressure driven and shear flows. However, there seem to be limited efforts in the literature to model multiparticle electrokinetic transport in bounded flows. To the author's best knowledge, there is no literature reported till date on the near wall electrokinetic transport of two or more particles in microchannels.

The present study aims to attain a clearer insight into the kinetics of particle transport and deposition in pressure driven and electrokinetic microchannel flows through a fundamental, systematic and deep exploration of the boundary effects on particle interactions and deposition in microchannels.

1.2 Objectives of the present study

From the above discussion, it is evident that, in order to achieve efficient design for Lab-on-a-chip microfluidic devices, a fundamental understanding of particle transport and deposition phenomena in microfluidic devices is inevitable. Also, parallel plate geometry is found to be favored in microfluidic devices due to its inherent simplicity. Therefore, the main objective of this study is to analyze particle transport and deposition from pressure driven and electrokinetic flow in parallel plate microchannels, accounting for the boundary effects on particle interactions. The objectives for this dissertation can be summarized as

- (1) Development of comprehensive numerical models describing particle transport and deposition from pressure driven and electrokinetic flow in parallel plate microchannels, which accounts for the interactions due to adsorbed particles. This can be attained by performing systematic study of the effect of electrolyte concentration, flow velocity, particle size etc. on particle transport and deposition.
- (2) Fabrication of parallel plate flow chamber and development of experimental set up to conduct videomicroscopic experiments for the quantification of particle deposition. Thorough experiments will be performed under various hydrodynamic and physicochemical conditions in order to validate the numerical simulation results.
- (3) In-depth exploration of the boundary effects on electrokinetic particle transport in parallel plate microchannels through an analytical study to understand the effect of geometrical and physicochemical parameters on particle transport in microchannels. The effects of electric field strength, particle-wall size ratio, particle and wall zeta potential, particle separation etc. will be studied in detail.

CHAPTER 1

1.3 Organization of the thesis

Chapter 1 is an introduction, which presents the background and inspiration for this work. The importance of electrokinetic transport and the significance of parallel plate geometry in microfluidic devices are stressed and the objectives of the project are outlined. A brief overview of the various mechanisms of colloidal particle transport and deposition in microchannels is provided. Furthermore, an account of the various particle deposition systems that are currently employed for particle deposition studies is given.

Chapter 2 presents an extensive review of the existing literature on particle transport and deposition from pressure driven and electrokinetic flows in microchannels. Analytical and numerical studies related to pressure-driven and electrokinetic particle transport in microchannels have been discussed elaborately.

Chapter 3 deals with the deterministic modeling of particle deposition from pressure driven flow in a parallel plate microchannel. The quantitative formulation of the mass transport equations is given in detail along with the explanation of numerical techniques to solve the problem. The Blocking function model and surface coverage calculation are elaborated. The design and development of the flow cell and the experimental set up are briefed. Finally, the theoretical predictions are compared with experiment and the results from the Blocking function model.

Chapter 4 presents the detailed mathematical modeling of Brownian dynamics simulation technique which is employed for modeling particle deposition from pressure

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driven and electrokinetic flows in parallel plate microchannels. Starting with the stochastic Langevin equation governing the particle motion, the colloidal and hydrodynamic interactions that control the particle transport and deposition on collector surfaces are elaborated, followed by a detailed description of the simulation algorithm. The parallel plate flow chamber design and the videomicroscopic imaging of particle deposition are described in detail. The theoretical predictions of surface coverage are compared with the experimental results and a brief discussion is provided regarding the agreement between theory and experiment.

The analytical modeling of electrokinetic transport of two spheres in a parallel plate microchannel is presented in **Chapter 5**. The mathematical model which involves Spherical harmonic functions and Complex Fourier integrals that represent the perturbations to the electrical potential and flow field by the spheres and the plane walls, is described in detail, starting with the governing equations for the applied electrical potential (Laplace equation) and fluid velocity (Stokes equation). Results for the axisymmetric and asymmetric motion one sphere and the asymmetric planar motion of two spheres in a microchannel are discussed in detail.

The major conclusions derived from the present study and the scope for future research is presented in **Chapter 6**. Significant contributions from this work are highlighted and the scope for future research is expanded.

1.4 Colloidal Particle transport and deposition

Transport and deposition are two vital aspects of the behavior of colloidal particles. An important aspect of the behavior of dispersed particles is their colloidal stability, which determines whether they remain in dispersed state or form deposits. Suspended particles can be deposited on a collector surface by two steps.

(a) Transport to the surface

(b) Irreversible attachment onto the surface

Hence, the deposition of colloidal particles on the collector surface is influenced by the transport near to the surface. At large distances from the collector surface, particle transport in the bulk fluid is determined by hydrodynamic convection, diffusion, brownian motion and migration due to external forces such as gravity. As a particle approaches the collector surface within a distance comparable to the particle size, displacement of the fluid between the particle and the collector becomes increasingly difficult because of additional hydrodynamic drag on the particle due to the presence of the collector surface. Hence, in the vicinity of the channel wall, the particle motion is retarded due to the presence of the wall. Similarly, the presence of the neighboring particles causes the retardation of a moving particle. These are referred to as “Hydrodynamic interactions”. Likewise, the diffusive motion of a particle is also affected by its neighboring particles and the wall, and consequently the particle diffusivity is deviated from the Stokes-Einstein diffusivity of a single particle. At even closer distances to the collector (1-100 nm), apart from the above-mentioned hydrodynamic interaction,

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the particle's motion is affected by colloidal forces: First, the universal van der Waals (VDW) forces become significant within such a range. Second, interfaces in aqueous media are nearly always charged due to the adsorption of ionic surface-active molecules or the dissociation of ionizable surface sites. Therefore, a so-called electric double layer (EDL) is formed within a region of the order of the Debye length. The EDL interaction may develop at such a region.

Fig 1.1 EDL development on a charged surface

Fig 1.1 represents the EDL development on charged surfaces. Oppositely charged ions (counter-ions) are attached to the charged surface and form an immobile layer (Stern layer). The layer above the stern layer is called the diffuse layer and it constitutes of both the counter-ions and co-ions (ions with the same type of charge as the surface) with the former more in number. Hence the EDL is not electrically neutral and is responsible for

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the electrical interactions. The thickness of EDL may range between (3-300)nm. EDL thickness is a parameter strongly dependent on the electrolyte solution concentration. The EDL interaction can be either attractive or repulsive depending on the nature of particle and surface charges. The van der Waals and the EDL interactions form the basis of the well-known Derjaguin-Landau-Verwey-Overbeek (DLVO) theory of colloidal stability. In addition, other non-DLVO colloidal interactions may be important to the kinetics of particle deposition under certain physicochemical conditions. These are short-range interactions (0.5-5)nm which may include hydration (structural), steric, hydrophobic, and polymer bridging interactions.

Stochastic effects such as flux due to discrete surface charges on the collector and particle surfaces, surface heterogeneity and roughness etc., may play pronounced roles when the particle is close to physical contact with the collector, which occurs at the so-called primary energy minimum (PEM) within (0.5-1.0)nm. Obviously, traditional continuum mechanics breaks down at such molecular dimensions.

1.5 Deposition systems

1.5.1 Rotating disc system

The rotating disc is a popular tool for studying the mass transfer and surface reactions in various engineering and applied science disciplines. The main reason for the broad use of this technique is the fact that the hydrodynamics of fluid motion near the disc surface is relatively simple and well known. Extensive theoretical and experimental work has been

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carried out in particle deposition on this geometry. The schematic view of Rotating disc system is presented in Fig 1.2.

Fig 1.2 Rotating disc system

A unique feature of this system is that the thicknesses of the hydrodynamic and diffusion boundary layers are constant over the entire surface of the disc. Hence, it is extensively used in studies of particle deposition. A major disadvantage is that Videomicroscopic observation of particles can not be employed for experimental studies of particle deposition because of the disk rotation.

1.5.2 Impinging jet cell system

The impinging jet-cell is referred to as the “stagnation point flow system” because of the presence of a stagnation point in the flow. Mass transfer in this type of flow has the same advantages of the rotating disc system. In addition, it is possible to observe the particles directly by microscopic means, which can not be done in rotating disc. Furthermore,

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particle deposition in stagnation point flow can provide a first approximation for deposition on more complex systems such as spherical and cylindrical collectors.

Fig 1.3 Impinging jet cell system

1.5.3 Parallel plate channel system

The parallel plate channel systems have been widely used in theoretical and experimental studies on particle deposition. Unlike the previous deposition systems, parallel plate channel system does not have a stagnation point. The hydrodynamic conditions in this case are more complex than rotating disc or stagnation point flow systems. A schematic of the parallel plate channel system is presented in Fig. 1.4. The quantitative formulation of the particle transport equation in a parallel plate channel is presented in Chapter 3. Parallel plate channel systems find enormous applications in the specialized field of microfluidics (e.g., Electrophoretic separation of bioparticles such as proteins in microchannels).

Fig 1.4 Parallel plate channel system

1.6 Contributions made by the present study

The important contributions made by this study can be summarized as,

- (1) Chapter 3 presented the deterministic modeling and experimental study of particle deposition from parallel plate microchannel flows. The particle deposition rate was quantified in terms of the Sherwood number, which represents the dimensionless flux at the collector surface. The theoretical results and the results from videomicroscopic experiments made reasonably good comparison for the range of physicochemical parameters chosen in the study. A blocking function based on Random Sequential Adsorption model (RSA) was also derived to analyze the effect of surface blocking on particle deposition. However, it was found that the Blocking function approach is inadequate to model deposition kinetics at high Reynolds numbers.
- (2) Chapter 4 describes the Brownian dynamics simulation and experimental study of particle deposition from pressure driven and electrokinetic flows, where no theoretical studies on particle deposition from electrokinetic flow exists to date. The simulation technique is based on the stochastic Langevin equation for particle motion, where the colloidal, hydrodynamic and Brownian forces on the particle motion are incorporated.

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The theoretical results in terms of surface coverage provided meaningful comparison with experimental data at high Reynolds numbers.

- (3) The motivation for the analytical study performed in Chapter 5 stems from the importance of boundary effects on particle transport in microfluidic devices. The analytical model helped in deriving a fundamental understanding of the electrokinetic particle transport of two spheres in bounded domain. Also, the model can be easily extended to multisphere problems. The electrokinetic transport of two spheres in a parallel plate microchannel is investigated through the formulation of an analytical model. The Laplace equation for the electrical potential and the Navier-Stokes equation for the flow field were solved through an approach involving the representation of the sphere and wall disturbances through spherical harmonic functions and Fourier integrals, respectively. The analytical results for the case of axisymmetric motion of a single sphere in a parallel plate microchannel are validated using the existing literature. Also, the eccentricity of particle motion in a microchannel enhances both the translational and rotational velocity. Furthermore, the theoretical results imply that, in the bulk fluid, particles with smaller size and larger zeta potential travel faster and can overtake larger particles or particles with lower zeta potential.

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LITERATURE REVIEW

2.1 Introduction

Transport and deposition of colloidal particles in microchannels plays an important role in many engineering and biochemical processes such as filtration, contamination control of microelectronic devices, particle separation in microfluidic devices, biofouling of artificial organs etc. This chapter elaborates the published work in the area of colloidal particle transport and deposition from pressure driven and electrokinetic microchannel flows. The deterministic and stochastic models governing particle deposition in microchannels are reviewed in detail, along with the optical techniques to measure particle deposition. A brief account of the analytical and numerical work on the boundary effects on the electrokinetic transport of colloidal particles is provided in view of the bioparticle transport and deposition in microfluidic devices.

2.2 Deterministic modeling of particle deposition

Adamczyk and van de Ven (1983) presented an approximate analytical solution of the kinetics of particle accumulation at collector surfaces. General continuity equations were formulated both for the mobile and immobile (adsorbed) colloids, with the appropriate initial and boundary conditions. These equations were integrated over regions of particle accumulation (energy minima), and expressed in terms of surface concentrations. Excellent reviews on particle deposition on collectors of various geometry from flowing suspensions were provided by Adamczyk et al. (1989). The “perfect sink model” was discussed in detail along with various effects influencing particle transfer including

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diffusion, convection, geometrical interception and migration under external forces (gravity).

Elimelech and O'Meila (1990) developed a theoretical framework for chemical-colloidal effects on the kinetics of deposition of Brownian particles in porous media. The theory was tested by conducting deposition experiments with model colloids and collectors under controlled chemical conditions in a well-defined experimental system. Experimental (collision) attachment efficiencies were calculated from measured particle deposition rates. A pronounced effect of particle size on attachment efficiencies was predicted by theory. DLVO theory for colloidal stability was found unsuccessful in predicting the kinetics of particle deposition through porous media. The effect of particle size on deposition under attractive double layer interactions was investigated by Elimelech et al. (1991, 1993). Mass transport equations were formulated incorporating van der Waals, EDL and hydrodynamic interactions and were solved numerically. The theoretical predictions were in good agreement with the experiment, and an increase in deposition rate was observed as the electrolyte concentration was reduced. This was termed "Inverse salt effect". More importantly, the enhancement in deposition rates (deposition rates in the presence of the double layer divided by deposition rates in the absence of EDL interactions) was found to be dependent on particle size.

Later, Song et al. (1995) analyzed particle deposition onto permeable surfaces. The convection – diffusion equation was formulated with the inclusion of lateral transport due to permeation drag, inertial lift and transport by van der Waals, EDL and Gravity forces.

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The effects of particle size, permeation velocity, solution ionic strength, cross flow velocity and particle density on the initial rate of particle deposition were investigated. The results indicated an interplay between the external forces, permeation drag and inertial lift as the mechanism of particle deposition.

Yang et al. (1998) provided an in-depth theoretical analysis of the kinetics of particle deposition from an impinging jet cell. Complete mass transport equations incorporating van der Waals, EDL interactions and gravity were solved numerically. The results demonstrated that the asymmetric EDL interaction, which has been ignored in previous studies, has an influence on particle deposition. Also, the particle deposition rates were demonstrated to be strongly dependent on the particle-collector interaction energy profiles.

2.3 Interparticle interactions and Blocking effects

The theoretical models discussed above focus on the initial stage of deposition process where particles deposit on bare (clean) surfaces. As colloids deposit onto stationary surfaces, surfaces are progressively covered with retained particles. Hence, the interaction of suspended particles with previously deposited particles becomes important in the particle deposition process and should be considered.

Fig 2.1 Blocking phenomena

For low surface coverages ($\theta < 0.2$) (surface coverage is defined as the ratio of the area covered by the deposited particles to the area of the collector surface), a limiting analytical expression for the surface coverage was presented by Johnson and Elimelech (1995) based on “Random sequential adsorption” (RSA). In their work, a Blocking function, which has a nonlinear dependence on the surface coverage, was introduced in contrast with the linear Langmuirian Blocking function used in earlier models. Later, an extension to the RSA model using “Ballistic deposition model” (BD) was considered by Senger et al. (2000) for the cases in which gravity plays an important role. The validity of RSA and BD models was discussed in detail using experimental results. For higher surface coverages, however RSA and BD models were proved to be inadequate.

To account for this, Adamczyk et al. (1995) used the sequential Brownian dynamics simulation method to model the kinetics of particle deposition in an impinging jet cell. The stochastic trajectory simulation method developed by Ansell and Dickinson (1986) was used for computing the particle surface coverage. Videomicroscopic experiments using monodisperse suspension of positively charged polystyrene latex particles and mica

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collector surfaces were performed for measuring the influence of flow intensity (shear rate) and solution concentration on particle adsorption kinetics. The simulation results were compared with experiments using polystyrene particles, and a reasonable agreement was obtained. It was shown that the surface blocking phenomena for spherical particles becomes analogous to elongated non-spherical particles for no-flow conditions.

Using Brownian dynamics simulation, Hutter (1999) identified the coagulation time scales in colloidal suspensions for various solid content ratios. The dependence of the time scales on the solid content and the colloidal interaction parameters was investigated to achieve a better understanding of the coagulation mechanisms. A similar work by Villalba and Sucre (2000) addressed the stability of oil-in-water emulsions using Brownian dynamics simulation technique. Recently, the deposition of Brownian particles onto the collector surfaces of porous media was investigated by Chang et al. (2003). The effect of the colloidal interaction potential on the collector efficiency was examined. In addition, Scholl et al. (2000) performed Brownian dynamics simulations to numerically simulate TIRM (Total Internal reflection microscopy) experiments for the motion of a sphere in a viscous fluid near to a wall.

Monte-Carlo simulations were performed by Adamczyk et al. (2000) to estimate the diffusion-controlled adsorption of colloidal particles and proteins. The bulk and surface transport equations were solved numerically. It was shown that the limiting adsorption regime occurs for proteins at surface coverage very close to the jamming value, becoming therefore difficult to detect due to limited experimental accuracy. Adamczyk et al. (2001)

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used RSA model to predict irreversible adsorption of colloid particles at surfaces pre-covered with smaller particles having the same sign of surface charge. Numerical simulations were performed to evaluate the initial flux of larger particles as a function of the surface coverage of smaller particles. It was found that the jamming surface coverage is very sensitive to particle size ratios exceeding 4. Theoretical predictions suggested that surface heterogeneity i.e., the presence of smaller sized contaminants or smaller particles invisible under microscope, can be quantitatively characterized by studying the larger particle adsorption and the structure of the monolayer.

Monte- Carlo simulation studies on colloidal adsorption on heterogeneous surfaces were performed by Adamczyk et al. (2002). The substrate surface of controlled heterogeneity was created by covering a homogeneous surface by adsorption sites (active centers) of a desired concentration. Adsorption was assumed to occur due to short-range attractive interactions if the colloidal particle contacted the center. The simulations were performed to determine the initial flux, adsorption kinetics and jamming coverage.

2.4 Coupling and Stochastic effects

In the models described above, the electrical and hydrodynamic interactions are assumed to be decoupled. This assumption becomes valid only for low flow rates. At higher flow velocities, the EDL and hydrodynamic interactions are coupled. The EDL around the particle gets distorted due to the flow and the ions get redistributed as the particle moves. The viscous and electric stresses on the particle create a repulsive force termed as “electrokinetic lift”. Moreover, the particle velocity is reduced by the surrounding cloud

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of ions. This phenomenon is called “electroviscous drag”. These effects become pronounced for particles with thick double layers. The above-mentioned electrokinetic phenomena are strongly dependent on the flow velocity of the suspension and hence, on the shear rate. Dukhin and van de Ven (1993) investigated the dynamics of a spherical particle surrounded by a thin EDL in shear flow. The EDL, concentration and hydrodynamic fields, which arise in the neighborhood of a charged spherical particle with a thin EDL in shear flow were calculated, together with electroviscous effect.

Experimental investigations of electrokinetic lift of a sphere freely rotating and translating in linear shear flow were performed by Bike et al. (1995a). Observations were carried out using $9.87\ \mu\text{m}$ and $5.2\ \mu\text{m}$ diameter polystyrene latex spheres in solutions of varying viscosity. It was found that the increase in the particle-wall separation distance upon the initiation of flow generally increases with particle zeta potential for a given fluid conductivity. However, the predictions of lift based on the existing lubrication theory were more than one order of magnitude weaker than gravity. This disagreement led to the refinement of the electrokinetic theory by Bike et al. (1995b). The numerical calculations were performed using the “lubrication approximation” assuming that the EDL thickness is sufficiently small and the space charge density is not perturbed by the flow. Still, there existed a discrepancy of one order of magnitude between theory and experiment.

This discrepancy was solved to an extent by Warszynski et al. (1998) in calculating the electrokinetic lift force on a particle near to a plane wall. The theory was based on the lubrication approximation for the solution of Stokes equations. Thin double layer

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assumption was used to solve ionic balance and electrosmotic flow equations and the lift force was obtained by the integration of the viscous stress tensor and the Maxwell stress tensor over the particle surface. A “colloidal collider” experiment employing latex particles and glycerol-water solutions was set up for experimental validation. The results from the theoretical calculations were orders of magnitude greater than the previous predictions by Bike and Prieve, and were in good agreement with experiment.

2.5 Experimental techniques

Numerous experimental techniques have been developed to study particle deposition (Bowen and Epstein (1979), Adamczyk et al. (1983), Elimelech et al. (1995) and Sanders et al. (1995)). The parallel-flow channel and the impinging jet cell are two widely used techniques for particle deposition experiment because of their numerous advantages such as well possessing controlled and characterized hydrodynamic flow, allowing direct observation of the deposition process by videomicroscopes etc.

Meinders et al. (1991) conducted the simultaneous monitoring of adsorption and desorption of colloidal particles during deposition in a parallel plate flow chamber. A phase contrast microscope was used with an ultra long working distance objective for the *in situ* measurement of deposition. The particle deposition rates were found to be strong functions of the resident time of the adhering particles.

The impinging jet cell technique pioneered by Dabros and van de Ven (1983, 1987) was used for characterizing polymer adsorption (Dijt et al. (1990)), particle detachment

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(Varennnes et al. (1987)), deposition of oil emulsion (Sanders et al. (1995)), and attachment of micron-sized bubbles (Yang et al. (2003)). Such a technique was improved by Adamczyk and his co-workers (Adamczyk et al. 2000, 2002).

Fattah and Genk (1998) investigated the adsorption of hydrophobic, negatively charged polystyrene latex microspheres onto a stagnant air/water interface. The measured variation of surface coverage and characteristic time of adsorption was attributed to the accessibility of the interface to sorbing particles determined by the combined effect of the energy barrier at the interface and that between particles in bulk solution.

Weiss et al. (1998) analyzed the mechanism of desorption kinetics (reversible adsorption) of colloidal particles at solid-liquid interfaces. The focus was kept on the time scale of desorption rather than the adsorption rate. Using evanescent field method and Videomicroscopy, the individual particle arrival and departure times were identified to determine the adhesion time distribution function.

Fattah et al. (2002a, 2002b) used a high-resolution optical Videomicroscopic system for image processing and data extraction of polystyrene colloids of diameter $0.3\ \mu\text{m}$. The system used a relatively large field of view ($330 \times 245\ \mu\text{m}$) and utilized dark-field microscopy to visualize colloids as small as $0.3\ \mu\text{m}$ in diameter at the surface and in the bulk suspension with a sufficient resolution ($\sim 0.5\ \mu\text{m}$). The extracted data include

- (i) Surface concentration and flux of deposited, attached and detached colloids.
- (ii) Surface concentration and flux of arriving and departing colloids.

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- (iii) Distribution of colloids in the bulk suspension in the direction perpendicular to the deposition surface.
- (iv) Spatial and temporal distribution of deposited colloids.

The above-discussed models assumed a homogeneous surface for adsorption. But, the experiments of Luthi and Ricka (1998a) revealed surprisingly complex results. The glass surface, though optically flat and well cleaned, is not homogeneous, but rather the adsorption occurs at a limited number of preferred sites. Moreover, these sites are not static. These findings were understood within a simple model that takes into account slow but inevitable dissolution of the glass surface. The bulk glass contained potential adsorbers which were continuously being exposed by the dissolution process and act as transient adsorption sites, before being washed off by the flowing buffer solution. The pros and cons of Videomicroscopic analysis of colloidal particle deposition were examined by Luthi and Ricka (1998b). Parallel plate channel geometry was selected and the adsorption was analyzed in the presence of a repulsive barrier. Special attention was paid to the kinetics of particle release, which was found to be highly non-exponential.

2.6 Boundary effects on particle interactions in microchannels

Extensive analytical and numerical studies on particle interactions in Stokes flow in the case of bounded and unbounded flows have been performed till date. An excellent review of these studies can be found in Weinbaum et al. (1990). Classical studies in low-Reynolds number hydrodynamics have focused on either (a) exact solutions in special orthogonal coordinate systems in which the Stokes equation is simply separable, (b) the

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method of reflections for more distant particle-boundary interactions (Happel and Brenner, 1973) or (c) Slender body theory (Batchelor 1970, Chwang and Wu, 1975).

Gluckman et al.(1972) used multipole collocation technique to model axisymmetric bounded flows, representing an arbitrary convex body of revolution using a distribution of oblate spheroidal singularities whose foci coincided with the surface of the body. The motion of an axial cluster of spheres inside a circular cylinder was considered by Leichtberg et al. (1976). In this study, a Fourier transform of the wall disturbance was analytically inverted to satisfy the no-slip conditions on the boundaries for an arbitrary distribution of Sampson singularities representing the velocity disturbance produced by the spheres. This basic methodology was extended to three dimensional planar motions involving either unbounded spheres (Ganatos et al. 1978) or a sphere moving between plane parallel walls (Ganatos et al. 1980a, 1980b, 1982). Further extension to this study was performed by Hassonjee et al. (1988) in considering the arbitrary motion of three dimensional clusters of unbounded spheres. It was found that the lowest order singularities in Lamb's spherical harmonic functions used to represent the velocity disturbance produce by each sphere, are identical to the point force, rotlet, and stresslet singularities used to describe the many-body interactions in the multipole moment method of Durlofsky et al. (1987) and Brady et al. (1988).

Although multipole collocation technique combined with internal singularity distributions has been very successful in representing arbitrary bodies of revolution in unbounded flow, the greater versatility of the boundary integral equation technique in treating three

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dimensional bodies and deformable interfaces has made the latter the preferred method for treating arbitrary body shapes. The basic theory developed by Ladyshenskaya (1963) for single and double layer potentials in Stokes flow was developed into a powerful numerical method for treating three dimensional Stoke's flows by Youngren and Acrivos (1975). In the initial application of this technique, the free space Green's function, or Stokeslet, was distributed over an arbitrary body in unbounded flow, which leads to a boundary integral equation for the single layer potential. For moving surfaces that bound a rigid body, the double layer potential, or stresslet integral, was eliminated by applying the divergence theorem (Rallison and Acrivos 1978). The boundary was then discretized and the unknown Stokeslet distribution determined by solving a matrix equation for all wall elements. An important feature of this approach is that the surface stress distribution and the drag and torque on the body can be determined without actually solving for the velocity field.

The most severe limitations of the boundary integral equation technique are its accuracy and the large amount of computer time required to evaluate singular integrals. Youngren and Acrivos (1975) used 144 discrete surface elements to describe the three dimensional flow past a prolate spheroid and obtained results for the force and torque in a shear flow that are accurate to within 1%; poorer accuracy is obtained for flows with rigid confining walls. In contrast, the three dimensional multipole solutions using Lamb's spherical harmonics and the multipole collocation technique (with only 14 collocation rings) on the surface of the sphere provided results with four digit accuracy for both unbounded

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(Hassonjee et al. 1988) and bounded (Ganantos et al. 1980b) flows at spacing up to $1/10$ of a diameter.

The abovementioned analytical and numerical techniques were applied extensively to the calculation of colloidal particle trajectories in microchannels. Dabros and van de Ven (1992) investigated the trajectories of a charged colloidal particle near to a plane wall in the vicinity of an attached particle in vertical sedimentation fields. The multi subunit and lubrication methods were employed for the computation of far field and near field hydrodynamic resistance. Later, a method for determination of interparticle colloidal forces was presented by van de Ven et al. (1994) based on experimental observation of the collision trajectories of two particles using a “Surface Collision Apparatus” and by a function minimization method. The relationship between the interparticle forces and the separation distance was expressed by a general function of the interparticle separation, with parameters determined from the best fit between theory and experiment. The multi subunit method developed by Dabros and van de Ven (1992) was employed for analyzing colloidal particle scattering in shear fields by Whittle et al. (2000). The mobility matrix method (Kim and Karrila, 1991) was employed to compute the particle velocities from the driving forces and the effect of the presence of exponential surface forces on particle trajectories was studied. The wall effect on the Brownian motion of a rigid colloidal particle in a viscous fluid was analyzed by Sholl et al. (2000). Brownian dynamics simulation was employed to numerically simulate TIRM (Total internal reflection Microscopy) experiments which are used to extract the potential energy profile of the particle from the observed Brownian motion.

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In the literature, numerous theoretical works have been reported on the electrophoretic transport of a single particle in bounded flows. The earlier analyses done by Keh and Anderson (1985), Keh and Chen (1988) and Keh and Lien (1991) investigated the boundary effects on the electrophoretic motion of a single colloidal particle moving parallel to a plane surface or through the axis of a circular orifice. These studies reported an increase in electrophoretic mobility of the particle in the vicinity of the wall. The particle velocity was found to increase by 23% of the particle velocity in an unbounded system when $\lambda = 0.995$, where λ represents the ratio of the particle radius to the distance from the boundary. This effect was attributed to an increase in electrical stresses as the particle approaches the plane wall, resulting in an increase in the driving force. Subsequently, Shugai and Carnie (1994), Zydney (1995) respectively obtained analytical solutions for the electrophoretic velocity of a charged sphere moving near to a plane charged wall, inside a spherical cavity and inside a circular cylindrical tube.

Ennis and Anderson (1997) studied the boundary effects on the electrophoretic transport of a spherical particle with arbitrary double layer thickness and low zeta potential. The boundary configurations considered include a single flat wall, a slit and a long cylindrical tube. Using a method of reflections the particle velocity was obtained in powers of λ . An important finding of this study is that the hindrance to the particle velocity is increased significantly as κa_p is reduced, where κa_p is the scaled double layer thickness and a_p is the particle radius.

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Ye and Li (2002) studied the electrophoresis of a sphere in a microchannel under the gravitational field. The balance between colloidal and external forces was considered to calculate the separation between the sphere and the channel surface. Recently, the electrophoretic motion of two spherical particles in a rectangular microchannel was numerically investigated by Ye and Li (2004). Their work focused on the boundary effect on the flow field and electric field surrounding the moving particles. It was found that smaller particles move slightly faster and will climb over a larger particles moving in front, if the centers of the particles are not located on the same line parallel to the applied electric field.

2.7 Key research needs and current deficiencies in knowledge relevant to the present study

This section is devoted to the understanding of the needs and deficiencies in knowledge related to the present work. Even though several studies have been conducted on the transport and deposition of particles in pressure driven flows, relatively little effort seem to have appeared in modeling the kinetics of particle deposition from electrokinetic flows, which bears prime importance to the design and operation of chip based microfluidic devices. In applications related to capillary electrophoresis systems, deposition of cells (of micrometer in size) on the channel wall with high surface coverage may not occur. However, for the cases of electrophoretic separation of proteins and DNA smaller particles, deposition of these small biomolecules (i.e., biofouling) is a severe unsolved problem. In addition, the present study is relevant to the development to so-called field-flow fractionation method that is a flow-assisted separation technique for separation and immobilization of analytes from macromolecules such as protein and DNA to micron-sized particles such as cells. Also, the operation of Biochips for cell/ particle handling

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operations normally encounter electrokinetic transport of particles that are comparable to the size of the channel wall. In such a situation, the need for the understanding of boundary effects on particle transport arises. A comprehensive mathematical model is needed to predict the effect electrohydrodynamic coupling interactions on the particle transport. In addition, the present study is relevant to the development to so-called field-flow fractionation method that is a flow-assisted separation technique for separation and immobilization of analytes from macromolecules such as protein and DNA to micron-sized particles such as cells (Du and Schimpf (2002)). Hence, the present work focuses on the kinetics of particle transport and deposition in pressure driven and electrokinetically driven microchannel flows through a fundamental, systematic and deep exploration of the boundary effects on particle interactions and deposition in microchannels. The potential applications of this study are related to the design and analysis of Lab-on-a-Chip devices, in which fundamental understanding of the underlying mechanisms behind the transport of bioparticles is crucial.

CHAPTER 3

DETERMINISTIC MODELING OF PARTICLE DEPOSITION FROM PRESSURE DRIVEN FLOW IN A MICROCHANNEL

3.1 Introduction

This chapter presents the deterministic modeling of colloidal particle deposition in a parallel plate microchannel and the subsequent experimental validation using parallel plate flow technique. This study is performed within the framework of the *DLVO* (Derjaguin-Landau-Verwey-Overbeek) theory and the motive is to understand the influence of physicochemical parameters on particle deposition and the effect of interparticle interactions (Blocking) at the later stages of particle deposition in parallel plate microchannels. The two dimensional mass transport equation incorporating colloidal and hydrodynamic interactions is derived and solved numerically using a finite difference method. An analytical expression for the blocking function is derived based on Random Sequential Adsorption (RSA) method. Using the parallel plate technique, experiments are conducted to measure the deposition of monodisperse polystyrene latex particles onto glass collector surface. For steady state deposition, dimensionless particle flux (Sherwood number) calculated from the numerical model are compared with the experiment. However, the interactions between attached and flowing particles influence deposition at the later stages. The effect of these interparticle interactions is elaborated by comparing the results from the Blocking function model with the experimental data.

3.2 Mass transport equations

Fig 3.1 Geometrical sketch of particle transport in parallel plate channel

Fig 3.2 Geometry showing the collector surface, particle size and the separation distance.

The parallel plate microchannel and the associated coordinate system are shown in Fig 3.1.

The mass conservation equation for the colloidal particle transport can be expressed as

$$\frac{\partial}{\partial x}(j_x) + \frac{\partial}{\partial y}(j_y) = 0 \quad (3.1)$$

where j_x and j_y represent the mass fluxes of particles in X and Y direction respectively.

In the absence of source and sinks and under steady conditions, the particle flux components can be expressed as

$$j_x = -D_x \frac{\partial n}{\partial x} + U_x n + \frac{D_x F_x n}{k_B T} \quad (3.2)$$

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$$j_y = -D_y \frac{\partial n}{\partial y} + U_y n + \frac{D_y F_y n}{k_B T} \quad (3.3)$$

where D_x and D_y represent the particle diffusivities in X and Y directions respectively, U_x and U_y are the particle velocities in X and Y direction, in the absence of diffusion and external forces, or in other words, the convective component of particle velocity. F_x and F_y represent the components of the total force acting on the particles, and $k_B T$ is the thermal energy ($k_B T$ represents the Boltzmann's constant). n represents the particle number concentration.

In the vicinity of the channel wall, the displacement of the fluid between the particle and the wall becomes increasingly difficult because of the additional hydrodynamic drag exerting on the particle (apart from the Stokes drag of a particle in the absence of a wall). Hence, in the vicinity of the channel wall, the particle motion is retarded due to the presence of the wall. Similarly, the presence of the neighboring particles causes the retardation of the moving particle. These are referred to as Hydrodynamic interactions (Elimelech et al. 1995). Hence, the particle velocity and diffusivity are affected by the presence of the wall. Correction functions, named as Universal Hydrodynamic Correction Functions (UHCC), are employed to account for the deviation of particle velocity and diffusivity from the values in bulk fluid. In this study, a 6mm wide and 0.3mm deep microchannel is used in the experiment, and hereby the width to depth ratio of the microchannel is 20; this allows us to assume a fully developed flow between two parallel plates. Hence, the particle velocity can be expressed as

$$U_x = f_3(H) \frac{3}{2} V_m \left[1 - \left(\frac{y}{B} \right)^2 \right] \quad (3.4)$$

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where $f_3(H)$ represents the correction function for the particle motion parallel to a plane wall. H represents the dimensionless particle-wall separation, expressed by

$$H = \frac{(B - y) - a_p}{a_p} \quad (3.5)$$

Similary, the particle diffusivities can be given as

$$D_x = f_4(H)D_\infty \quad D_y = f_1(H)D_\infty \quad (3.6)$$

where $f_4(H)$ and $f_1(H)$ represent the correction functions for the diffusive motion of a sphere near to a plane wall and D_∞ is the Stokes-Einstein diffusivity, expressed as $D_\infty = k_B T / 6\pi\mu a_p$. In this equation, μ represents the dynamic viscosity of the fluid and a_p is the particle radius.

Empirical expressions for $f_1(H)$, $f_3(H)$ and $f_4(H)$ are given by Masliyah (1994),

$$f_1(H) = 1 - 0.399 \exp(-0.14869H) - 0.601 \exp(-1.2015H^{0.92667}) \quad (3.7a)$$

$$f_3(H) = 1 - 0.3752 \exp(-3.906H) - 0.625 \exp(-3.105H^{0.15}) \quad (3.7b)$$

$$f_4(H) = 1 - 1.23122 \exp(-0.2734H) + 0.8189 \exp(-0.175H^{1.2643}) \quad (3.7c)$$

In the present model, a parallel plate channel of height $2B$ is considered. The flow velocity is represented by the Reynolds number, Re which is defined on the basis of the mean flow velocity through the channel. The Peclet number, which measures the relative strength of convection to the diffusive motion of the particle, is defined based on the mean flow velocity and the particle radius. The particle concentration is non-dimensional

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zed using the bulk particle concentration, n_∞ . These dimensionless parameters are expressed as

$$\bar{x} = \frac{x}{L}, \quad A_p = \frac{a_p}{B}, \quad \bar{n} = \frac{n}{n_\infty}, \quad \text{Re} = \frac{\rho V_m L_c}{\mu}, \quad \text{Pe} = \frac{V_m a_p}{D_\infty} \quad (3.8a)$$

$$\bar{F}_i = \frac{F_i}{(k_B T / a_p)}, \quad \bar{j}_i = \frac{a_p j_i}{n_\infty D_\infty} \quad (3.8b)$$

In the above equation, $\bar{j}_i$ represents the dimensionless mass flux and $\bar{x}$ is the dimensionless channel length. The flow Reynolds number is defined based on the characteristic length, L_c . $L_c = 4B$, for fully developed flow between parallel plates.

Utilizing the expressions in equations (3.8a) and (3.8b) in equations (3.2) and (3.3), the dimensionless mass flux terms are expressed as

$$\bar{j}_x = -f_4(H) \frac{a_p}{L} \frac{\partial \bar{n}}{\partial x} + \frac{3}{2} f_3(H) \text{Pe} \left\{ 1 - [1 - A_p(1+H)]^2 \right\} \quad (3.9)$$

$$\bar{j}_y = -f_1(H) \frac{\partial \bar{n}}{\partial H} + f_1(H) \bar{F}_y \bar{n} \quad (3.10)$$

Equation (3.1) can be written in dimensionless form as

$$\frac{1}{L} \frac{\partial \bar{j}_x}{\partial x} - \frac{1}{a_p} \frac{\partial \bar{j}_y}{\partial H} = 0 \quad (3.11)$$

Equation (3.9) and (3.10) can be substituted in equation (3.11) to obtain

$$\begin{aligned} & \frac{1}{L} \frac{\partial}{\partial x} \left(-f_4(H) \frac{a_p}{L} \frac{\partial \bar{n}}{\partial x} \right) + \frac{2}{3L} f_3(H) \text{Pe} \left\{ 1 - [1 - A_p(1+H)]^2 \right\} \frac{\partial \bar{n}}{\partial x} \\ & - \frac{1}{a_p} \frac{\partial}{\partial H} \left(-f_1(H) \frac{\partial \bar{n}}{\partial H} + f_1(H) \bar{F}_y \bar{n} \right) = 0 \end{aligned} \quad (3.12)$$

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It has to be noted that, in the above equation, the ratio a_p / L^2 , which represents the ratio of the particle radius to the square of the channel length. As $L \gg a_p$, the tangential diffusion term in equation (3.12) can be safely neglected. However, this doesn't imply that $\frac{\partial^2 \bar{n}}{\partial x^2} = 0$. Hence $\bar{n}$ should not be considered as linear in $\bar{x}$.

Hence, the final particle transport equation can be written as

$$\frac{2f_3(H)Pe}{3L} \left\{ 1 - [1 - A_p(1+H)]^2 \right\} \frac{\partial \bar{n}}{\partial x} - \frac{\partial}{\partial H} \left(-f_1(H) \frac{\partial \bar{n}}{\partial H} + f_1(H) \bar{F}_y \bar{n} \right) = 0 \quad (3.13)$$

Equation (3.13) can be expanded as

$$\begin{aligned} & \frac{2f_3(H)Pe}{3L} \left\{ 1 - [1 - A_p(1+H)]^2 \right\} \frac{\partial \bar{n}}{\partial x} - f_1(H) \frac{\partial^2 \bar{n}}{\partial H^2} - \frac{df_1(H)}{dH} \frac{\partial \bar{n}}{\partial H} \\ & + \frac{df_1(H)}{dH} \bar{F}_y \bar{n} + f_1(H) \frac{d\bar{F}_y}{dH} \bar{n} + f_1(H) \bar{F}_y \frac{\partial \bar{n}}{\partial H} = 0 \end{aligned} \quad (3.14)$$

3.3 Colloidal and External forces

The colloidal forces considered in the present model include the van der Waals and Electrostatic double layer (EDL) forces that form the basis of the Derjaguin-Landau-Verwey-Overbeek (*DLVO*) theory of colloidal stability, developed independently by Derjaguin and Landau (1941) and Verwey and Overbeek (1948). The van der Waals force acts on the surface of the particle and is related to the distance between the particle and the collector surface inversely by power law expression. Hence this force decays fast at greater particle-collector separations. The EDL forces decay exponentially. Essentially,

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the van der Waals and EDL interactions are assumed to be additive, and combined to give the total interaction energy between particles as a function of separation distance.

Hence, the total force on the particle is expressed as

$$F = F_{VDW} + F_{EDL} + F_G \quad (3.15)$$

where F_{VDW} , F_{EDL} and F_G are Van der Waals, EDL and Gravity forces respectively.

3.3.1 Van der Waals interactions

The attraction between two closely separated surfaces is generally called the London-van der Waals force. The force arises from spontaneous electrical and magnetic polarizations, giving a fluctuating electromagnetic field within the media and in the gap between them. Essentially, there are two theoretical approaches to evaluation of the van der Waals interaction. In the classical (or microscopic) approach, the interaction between two macroscopic bodies is obtained by the pairwise summation of all the relevant intermolecular interactions. All expressions obtained in this manner may be split into a purely geometrical part and a constant A , the Hamaker constant, which is related only to the properties of the interacting macroscopic bodies and the medium. Typically, A lies between $10^{-21} J$ and $10^{-19} J$. Hamaker's method can be easily applied to different geometries. However, the assumption of complete additivity is a rather serious deficiency and the resulting expressions always overestimate the interaction. The additivity assumption is overcome through the use of an alternative (macroscopic) approach suggested by Lifshitz et al. (1956), in which the interaction is derived entirely from

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consideration of the macroscopic electromagnetic properties of the medium. In spite of its rigor, extensive application of the theory has so far been hampered because of

1. The difficulty in obtaining adequate experimental data on the frequency-dependent dielectric permittivity of the colloidal particles and of the solvent medium, and
2. The prohibitive difficulty in its formulation for geometries other than the simplest plate – plate arrangement.

The Hamaker expressions are based on the pairwise additivity of intermolecular forces. The interaction between two particles is calculated simply by summing the interactions of all molecules in one particle with all of the molecules in the other. Hamaker et al. (1937) replaced the summation by a double integration procedure, which leads to very simple expressions. For two spheres of radii a_1 and a_2 , separated by a distance h , the interaction energy at close approach ($h \ll a_p$) is given by equation (3.16).

$$V_A = -\frac{A_{12}a_1a_2}{6h(a_1 + a_2)} \quad (3.16)$$

where A_{12} is the Hamaker constant for the media 1 and 2, of which the spheres are composed, and assuming that they are immersed in vacuum. This depends entirely on the properties of the interacting media. For equal spheres of radius a_1 , the result is simply given by equation (3.17).

$$V_A = -\frac{A_{11}a_1}{12h} \quad (3.17)$$

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These expressions only apply at close approach and become quite inaccurate at separations greater than about 10% of the particle radius. However, in many cases, the interaction energy is insignificant at larger distances. Hence, these expressions can be conveniently used for calculations. The most important feature of the Hamaker expressions includes the inverse dependence of the interaction energy on separation distance, and the direct dependence on particle size.

The same expressions can be used for the evaluation of Hamaker constant for interactions through liquid as encountered in problems of colloidal stability and deposition. The Hamaker constant for media 1 and 2 separated by medium 3 can be written as

$$A_{132} = A_{12} + A_{33} - A_{13} - A_{23} \quad (3.18)$$

A useful approximation for Hamaker constants of different media is the geometrical mean assumption

$$A_{ij} \approx \sqrt{A_{ii} A_{jj}} \quad (3.19)$$

Hence, equation (3.18) becomes

$$A_{132} \approx \left(\sqrt{A_{11}} - \sqrt{A_{33}} \right) \left(\sqrt{A_{22}} - \sqrt{A_{33}} \right) \quad (3.20)$$

For similar materials, 1, interacting across medium 3, the Hamaker constant can be given as

$$A_{131} = \left(\sqrt{A_{11}} - \sqrt{A_{33}} \right)^2 \quad (3.21)$$

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Equation (3.21) leads to the conclusion that the van der Waals interaction between similar materials in a liquid would always be attractive (i.e., positive Hamaker constant).

Since dispersions are electromagnetic in character, they are subject to a retardation effect. The finite time of propagation causes a reduced correlation between oscillations in the interacting bodies and a smaller interaction. The characteristic wavelength of the interaction can be expressed as

$$\lambda = \frac{2\pi c}{\omega_v} \quad (3.22)$$

where c is the velocity of light and ω_v is the dispersion frequency. λ has a value of around 100nm for most materials. It is often assumed that retardation comes into play when the separation distance between particles is of the same order as the characteristic wavelength.

The dimensionless form of Van der Waals interaction force between a sphere and a flat plate is expressed as (Yang et al., 1998),

$$\overline{F}_{VDW} = -Ad \frac{\overline{\lambda}(\overline{\lambda} + 22.232H)}{H^2(\overline{\lambda} + 11.116H)^2} \quad (3.23)$$

where $\overline{\lambda} = \frac{\lambda}{a_p}$.

Ad is named as Adhesion number, which is defined as

$$Ad = \frac{A}{6k_B T} \quad (3.24)$$

CHAPTER 3**3.3.2 EDL interactions**

When two charged particles approach each other, in an electrolyte solution, their diffuse double layers overlap and, in the case of similarly charged particles, repulsion is experienced between them. The precise way in which the double layers respond to each other depends on a number of factors. One distinction, which was recognized early in colloidal stability theory, is between interactions at constant surface potential or constant surface charge density. The former case corresponds to the maintenance of surface-chemical equilibrium during approach, which, because of the very short time of an encounter between colloidal particles may not be a realistic assumption (Frans and Overbeek, 1972). Constant – charge interaction might be expected when the particles have a fixed surface charge density. These considerations apply to the potential and charge at the particle surface, whereas double layer interaction depends on the potential at the stern plane, which may respond differently to the approach of another surface. The interaction energy may be calculated in two ways. One way is to solve the Poisson – Boltzmann equation directly for the system under consideration, but that is usually unable to give a simple analytical solution. The other method is to construct the formula from known expressions for each of the surfaces involved in the absence of the others. The approximations obtained in this manner are often of more practical importance because they are simple, yet fairly accurate.

3.3.2.1 Plate – plate interactions

A general formula for the force per unit area between two approaching flat double layers in a symmetrical ($z - z$) electrolyte was given by Langmuir et al. (1938) and Bell and

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Peterson(1972),

$$f_R = n_\infty k_B T \left[2 \cosh \phi - \left(\frac{d\phi}{\kappa dx} \right)^2 - 2 \right] \quad (3.25)$$

where n_∞ is the bulk number density of ions and $\phi = \frac{ze\varphi}{kT}$ and φ denotes the potential at a distance x from the plate. κ is the double layer thickness expressed as

$$\kappa = \sqrt{\frac{2z^2 e^2 n_\infty}{\epsilon k T}} \quad (3.26)$$

In the above equation, z represents the ionic valency, e is the fundamental electron charge and ϵ is the permittivity of the medium.

Integration of the force over distance then gives the potential energy per unit area, ν_R .

$$\nu_R = - \int_{\infty}^h f_R dx \quad (3.27)$$

where h is the separation between the two surfaces. At equilibrium, f_R should be equal everywhere, and the potential and the potential gradient can be computed from equation (3.25). A simple expression, which represents a useful compromise between the two extremes (constant potential and constant surface charge density), is the so-called linear superposition approximation (LSA). The LSA assumes that a region exists between the two interacting surfaces where the potential is sufficiently small and obeys the linearized Poisson– Boltzmann equation, so that contributions from each surface can be added to give the overall potential. In the vicinity of each surface, the potential is assumed to be due to that surface alone.

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3.3.2.2 Sphere – sphere interactions

In calculating the sphere – sphere double layer interactions, the most commonly used method is the integration method of Derjaguin et al. (1934). This is based on the corresponding plate– plate expression which is then used to construct the interaction energy between two closely spaced spheres.

$$V_R = \frac{2\pi a_1 a_2}{a_1 + a_2} \int_h^\infty \psi_R dx \quad (3.28)$$

The force of interaction, F_R ,

$$F_R = \frac{2\pi a_1 a_2}{a_1 + a_2} \psi_R(h) \quad (3.29)$$

where h denotes the minimum surface to surface separation between the spheres, and a_1 and a_2 are the radii of the spheres. The major disadvantage of this method is that it may be applied only when both the conditions $\kappa a_p > 5$ and $h \ll a_p$ are satisfied. Generally, $\kappa a_p > 5$ is considered to be adequate. The sphere-plate interactions can be estimated from sphere – sphere interactions by allowing one of the radii to approach infinity.

The dimensionless form of EDL force employed in the present study can be expressed as (Hogg et al., 1966),

$$\bar{F}_{EDL} = \kappa a_p D l \left(\frac{\exp(-\kappa h)}{1 + \exp(-\kappa h)} - Da \frac{\exp(-2\kappa h)}{1 - \exp(-2\kappa h)} \right) \quad (3.30)$$

The dimensionless groups in the above equation is defined as

$$Dl = \frac{4\pi\epsilon_0\epsilon_r a_p \zeta_p \zeta_w}{k_B T} \quad \text{and} \quad Da = \frac{(\zeta_w - \zeta_p)^2}{k_B T} \quad (3.31)$$

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The above equation is referred to as HHF expression (named after Hogg, Healy and Fuerstenau) which is based on constant potential interaction between the sphere and the flat plate. DI is the double layer parameter. Positive value of DI implies repulsive interaction and negative value implies attractive interaction. Da is the double layer asymmetry parameter accounting for the difference in surface potentials. In the above equation, ζ_w and ζ_p are the channel wall and particle zeta potentials. It should be noted that equation (3.30) is only valid for small zeta potentials ($|\zeta_p|, |\zeta_w| < 60mV$) and large values of $\kappa a_p > 5$.

3.3.3 External forces

Finally, the dimensionless gravity force (Gravity number) is defined as

$$\bar{F}_G = \frac{F_G}{(k_B T / a_p)} = -\frac{4\pi a_p^4 (\rho_p - \rho_f) g}{3k_B T} \quad (3.32)$$

where ρ_p and ρ_f are the particle and fluid densities, respectively.

3.4 Two dimensional model

In the two-dimensional model, $\bar{n}$ is considered as a function of both H and $\bar{x}$. The general form of equation (3.14) is expressed as

$$P_1(H) \frac{\partial \bar{n}}{\partial x} + P_2(H) \frac{\partial^2 \bar{n}}{\partial H^2} + P_3(H) \frac{\partial \bar{n}}{\partial H} + P_4(H) \bar{n} = 0 \quad (3.33)$$

The coefficients of equation (3.33) are expressed as,

$$P_1(H) = \frac{2}{3L} f_3(H) Pe \left\{ 1 - [1 - A_p (1 + H)]^2 \right\} \quad (3.34)$$

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$$P_2(H) = -f_1(H) \quad (3.35)$$

$$P_3(H) = f_1(H)\bar{F}_y - \frac{df_1(H)}{dH} \quad (3.36)$$

$$P_4(H) = f_1(H)\frac{d\bar{F}_y}{dH} + \frac{df_1(H)}{\partial H}\bar{F}_y \quad (3.37)$$

The boundary conditions for the solution of equation (3.33) can be given as

$$\bar{n} = 1 \text{ at } \bar{x} = 0 \quad (3.38)$$

$$\bar{n} = 0 \text{ at } H = H_0 \quad (3.39)$$

$$\bar{n} = 1 \text{ at } H = H_\infty \quad (3.40)$$

The first boundary condition expressed by equation (3.38) states that the inlet particle concentration is equal to the bulk particle concentration. In the second boundary condition, H_0 represents the closest particle-wall separation (dimensionless) and it is assumed that the particles are irreversibly captured when this separation is reached. This is referred to as the perfect sink approximation, widely used in particle deposition studies (Adamczyk et al. 1983). The third boundary condition states that the particle concentration reaches its bulk value when the particle is sufficiently far from the walls, represented by H_∞ in the dimensionless form.

Equation (3.33) is a homogeneous, linear parabolic partial differential equation. The equation is stiff, and can be solved only by using numerical techniques. The VDW and EDL forces are rapidly varying functions especially in the vicinity of the channel surface. Also, the range of integration of the functions varies from $H_0 = 0.001$ to $H_\infty = 100$. Hence the mesh size used for the finite difference approximation should be variable with

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smaller mesh size near to the channel surface and larger mesh size towards the bulk stream. Proper transforming functions can be used to overcome this difficulty. The transforming functions convert the variable mesh size in the physical grid to uniform mesh size in the computational grid. The accuracy of numerical solution can be improved by simply altering the constant mesh size. The new variables, designated as α and β , are given as

$$\alpha = \frac{\ln\left(\frac{H}{H_0}\right)}{\ln\left(\frac{H_\infty}{H_0}\right)} \quad \text{i.e., } H = H(\alpha) \quad (3.41)$$

$$\beta = \bar{x}$$

Using the above transforming functions, equation (3.33) becomes

$$G_1(\alpha) \frac{\partial \bar{n}}{\partial \beta} + G_2(\alpha) \frac{\partial^2 \bar{n}}{\partial \alpha^2} + G_3(\alpha) \frac{\partial \bar{n}}{\partial \alpha} + G_4(\alpha) \bar{n} = 0 \quad (3.42)$$

The transformed boundary conditions are now given as

$$\bar{n}(\alpha, \beta)_{\beta=0} = 1 \quad 0 \leq \alpha \leq 1 \quad (3.43a)$$

$$\bar{n}(\alpha, \beta)_{\alpha=1} = 1 \quad 0 \leq \beta \leq 1 \quad (3.43b)$$

$$\bar{n}(\alpha, \beta)_{\alpha=0} = 0 \quad 0 \leq \beta \leq 1 \quad (3.43c)$$

The functions $G_i(\alpha)$ and $P_i(\alpha)$ in equation (3.42) are expressed as

$$G_1(\alpha) = P_1(\alpha) \quad (3.44a)$$

$$G_2(\alpha) = -D_1^2 P_2(\alpha) \quad (3.44b)$$

$$G_3(\alpha) = D_1 P_3(\alpha) - D_2 P_2(\alpha) \quad (3.44c)$$

$$G_4(\alpha) = P_4(\alpha) \quad (3.44d)$$

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$$P_1(\alpha) = \frac{2f_3(\alpha)\text{Pe}}{3L} \left\{ 1 - \left[1 - A_p(1+H) \right]^2 \right\} \quad (3.44e)$$

$$P_2(\alpha) = f_1(\alpha) \quad (3.44f)$$

$$P_3(\alpha) = f_1(\alpha)\overline{F}_y(\alpha) - \frac{df_1(\alpha)}{d\alpha} \quad (3.44g)$$

$$P_4(\alpha) = f_1(\alpha)\frac{d\overline{F}_y(\alpha)}{d\alpha} + \overline{F}_y(\alpha)\frac{df_1(\alpha)}{d\alpha} \quad (3.44h)$$

$$D_1 = \frac{d\alpha}{dH} = \frac{1}{H \ln\left(\frac{H_\infty}{H_0}\right)} \quad (3.44i)$$

$$D_2 = \frac{d^2\alpha}{dH^2} = \frac{-1}{H^2 \ln\left(\frac{H_\infty}{H_0}\right)} \quad (3.44j)$$

$$\overline{F}_y(\alpha) = \overline{F}_y(H(\alpha)) \quad (3.44k)$$

where $f(\alpha) = f[H(\alpha)]$

Equation (3.42) is a typical parabolic second-order linear homogeneous PDE of convection-diffusion problem which can be solved by the well-known Crank-Nicolson method. Based on this scheme, the first order derivative n_α (from now, $\bar{n}$ is denoted as n for simplicity) at the mid grid point, $n_{(i,j+0.5)}$ can be approximated by the second-order centered difference approximation. The second order derivative $n_{\alpha\alpha}$ can be approximated by the average value of the second-order centered space expression. The method requires six points in every calculation step. Crank-Nicolson method is convergent irrespective of the mesh size. Hence the choice of mesh size is purely based on accuracy considerations. Equation (3.42) can be expressed in finite difference form suitable for numerical computation.

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$$G_1(j) \left[\frac{n_{j,i+1} - n_{j,i}}{\Delta\beta} \right] + \frac{G_2(j)}{2} \left[\frac{n_{j+1,i} - 2n_{j,i} + n_{j-1,i}}{\Delta\alpha^2} + \frac{n_{j+1,i+1} - 2n_{j,i+1} + n_{j-1,i+1}}{\Delta\alpha^2} \right] \\ + \frac{G_3(j)}{2} \left[\frac{n_{j+1,i} - n_{j-1,i}}{2\Delta\alpha} + \frac{n_{j+1,i+1} - n_{j-1,i+1}}{2\Delta\alpha} \right] + G_4(j) \left[\frac{n_{j,i} + n_{j,i+1}}{2} \right] = 0 \quad (3.45)$$

$$C_1(j)n_{j+1,i+1} + C_2(j)n_{j,i+1} + C_3(j)n_{j-1,i+1} + C_4(j)n_{j+1,i} + C_5(j)n_{j,i} + C_6(j)n_{j-1,i} = 0 \quad (3.46)$$

where

$$C_1(j) = \frac{G_2(j)}{2\Delta\alpha^2} + \frac{G_3(j)}{4\Delta\alpha} \quad (3.47a)$$

$$C_2(j) = \frac{G_1(j)}{\Delta\beta} - \frac{G_2(j)}{\Delta\alpha^2} + \frac{G_4(j)}{2} \quad (3.47b)$$

$$C_3(j) = \frac{G_2(j)}{2\Delta\alpha^2} - \frac{G_3(j)}{4\Delta\alpha} \quad (3.47c)$$

$$C_4(j) = \frac{G_2(j)}{2\Delta\alpha^2} + \frac{G_3(j)}{4\Delta\alpha} \quad (3.47d)$$

$$C_5(j) = \frac{-G_1(j)}{\Delta\beta} - \frac{G_2(j)}{\Delta\alpha^2} + \frac{G_4(j)}{2} \quad (3.47e)$$

$$C_6(j) = \frac{G_2(j)}{2\Delta\alpha^2} - \frac{G_3(j)}{4\Delta\alpha} \quad (3.47f)$$

Fig 3.3 Crank – Nicolson scheme

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In the computational domain, the Finite difference equations can be represented by a set of linear equations

$$j = 2, i = 1$$

$$C_1(2)n_{3,2} + C_2(2)n_{2,2} + C_3(2)n_{1,2} + C_4(j)n_{3,1} + C_5(2)n_{2,1} + C_6(2)n_{1,1} = 0 \quad (3.48a)$$

.....

$$j = j_{\max} - 1, i = 1$$

$$C_1(j_{\max} - 1)n_{j_{\max},2} + C_2(j_{\max} - 1)n_{j_{\max}-1,2} + C_3(j_{\max} - 1)n_{j_{\max}-2,2} + C_4(j_{\max} - 1)n_{j_{\max},1} + C_5(j_{\max} - 1)n_{j_{\max}-1,1} + C_6(j_{\max} - 1)n_{j_{\max}-2,1} = 0 \quad (3.48b)$$

Equation (3.46) can be rearranged to the general form

$$n_{j+1,i+1} = \frac{C_2(j)n_{j,i+1} + C_3(j)n_{j-1,i+1} + C_4(j)n_{j+1,i} + C_5(j)n_{j,i} + C_6(j)n_{j-1,i}}{-C_1(j)} \quad (3.49)$$

The procedure of numerical calculation is explained as follows. The values of $n_{j,i}$ at $i = 2$ can be computed using equation (3.49) from the known values of n at flow inlet i.e., $n_{j,1}$, if a guess value is provided for $n_{2,2}$. The value of $n_{2,2}$ is corrected till $n_{j_{\max},2}$ is as close to unity as possible. Using this iterative procedure, the values of n at all levels of i can be calculated using guess values for $n_{2,i}$.

The values of $\bar{n}(\alpha, \beta)$ determined in the computational domain can be transformed back to the physical domain using the relation,

$$H = H_0 \left(\frac{H_{\infty}}{H_0} \right)^{\alpha} \quad (3.50)$$

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The non-dimensional particle flux to the collector surface is quantified by the Sherwood number, Sh which can be expressed as

$$Sh = \frac{\left| (j_{\perp})_{H_0} \right|}{\left(\frac{D_{\infty} n_{\infty}}{a_p} \right)} = f_1(H_0) \left(\frac{d\bar{n}}{dH} \right)_{H=H_0} \quad (3.51)$$

where $(j_{\perp})_{H_0}$ represents the collector surface flux at $H = H_0$, which is represented as

$$j_{\perp} = \left(-f_1(H) \frac{d\bar{n}}{dH} + f_1(H) \bar{F}_y \bar{n} \right)_{H_0} = \left(-f_1(H) \frac{d\bar{n}}{dH} \right)_{H_0} \quad (3.52)$$

since, $\bar{n} = 0$ at $H = H_0$

The negative sign on the right hand side of equation (3.52) shows that the particle mass flux is toward the collector surface.

In the present study, computational tests were performed to estimate the influence of the choice of H_0 on the numerical results. It was found that the results are insensitive to the choice of H_0 as long as $H_0 \leq 0.002$ and $H_{\infty} > 50$. This means that a doubling of the lower or upper integration limits causes a change in the calculated values no more than 0.2%. Hence, in the numerical computation, the lower and upper H limits were selected to be $H_0 = 0.001$ and $H_{\infty} = 80$.

3.5 Surface Blocking and Blocking function model

Particle deposition deviates from the linear behavior after a certain period of time. This can be attributed to the repulsive interactions between depositing and deposited particles, preventing the deposition of further particles onto the surface. This phenomenon is named

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as “Blocking effect” (Johnson and Elimelech, 1995). Blocking depends on a number of factors such as flow velocity, surface coverage of particles, thickness of EDL layer around the particle etc. One of the effective ways to analyze the blocking effects is by “Random sequential Adsorption” (RSA) method. In the RSA method, the trajectory of a particle is not followed, but the probability of adsorption on a given spot at the interfaces is evaluated taking into account of the interactions between the neighboring particles. The probability of adsorption at a surface covered with particles is denoted as $B(\theta)$ which is also called “Available surface function” (Warszynski et al. 2000). θ represents the dimensionless surface coverage expressed as

$$\theta = \frac{\pi a_p^2 n_d}{\Delta S} \quad (3.53)$$

In the above equation, n_d represents the number of deposited particles (surface concentration) and ΔS is the area of adsorption.

The theoretical adsorption rate can be written as

$$\frac{dn_d}{dt} = j_{\perp} \quad (3.54)$$

where $j_{\perp}$ is the dimensionless particle flux to the channel surface (expressed by equation (3.52)).

The adsorption rate equation for a covered surface in the absence of desorption can be written as given by Warszynski (2000),

$$\frac{d\theta}{d\tau} = B(\theta) \quad (3.55)$$

$$\text{where } \tau = \frac{\pi a_p^2 j_{\perp} t}{0.547} = \frac{t}{t_{ch}} \quad (3.56)$$

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In the above equation, the factor 0.547 represents the maximum surface coverage attainable in the case of adsorption of hard spheres (spheres that are not interacting electrically) using RSA. This implies that $t_{ch} = \frac{0.547t}{\pi a_p^2 j_\perp}$, is the characteristic time for maximum adsorption on the collector surface (Warszynski et al., 2000).

In the case of low surface coverages and negligible flow velocities, a polynomial expression for $B(\theta)$ was given by Johnson and Elimelech (1995),

$$B(\theta) = 1 - C_1\theta + C_2\theta^2 + O(\theta^3) \quad (3.57)$$

In the above equation, the coefficients C_1 and C_2 for electrically interacting particles are expressed as (Adamczyk et al. 1995),

$$C_1 = 4(1 + H^*)^2 \quad (3.58)$$

$$C_2 = \frac{6\sqrt{3}}{\pi}(1 + H^*)^4 \quad (3.59)$$

where H^* is expressed as (Ko et al. 2000),

$$H^* = \frac{1}{\kappa a_p} \left[\ln(\xi) - \ln \left(1 + \frac{1}{2\kappa a_p} \ln(\xi) \right) \right] \quad (3.60)$$

where κa_p is the dimensionless EDL thickness.

$$\xi = \frac{8\epsilon_0\epsilon_r k_B T a_p}{20e^2} \tanh^2 \left(\frac{e\zeta_p}{kT} \right) \quad (3.61)$$

where e is the fundamental charge.

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Hence, equation (3.55) becomes

$$\frac{d\theta}{1 - C_1\theta + C_2\theta^2} = d\tau \quad (3.62)$$

Equation (3.62) has the form,

$$\frac{d\theta}{a\theta^2 + b\theta + c} = d\tau \quad (3.63)$$

where

$$a = \frac{6\sqrt{3}}{\pi}(1 + H^*)^4, \quad b = -4(1 + H^*)^2 \quad (3.64)$$

Integration of equation (3.63) results in

$$\frac{1}{\sqrt{b^2 - 4ac}} \ln \left[\frac{2a\theta + b - \sqrt{b^2 - 4ac}}{2a\theta + b + \sqrt{b^2 - 4ac}} \right] = \tau + C_I \quad (3.65)$$

The integration constant C_I can be evaluated from the condition,

$$\tau = 0, \quad \theta = 0 \quad (3.66)$$

The above boundary condition implies that at time $t = 0$, the particle surface coverage, $\theta = 0$.

$$\text{Hence, } C_I = \frac{1}{\sqrt{b^2 - 4ac}} \ln \left(\frac{b - \sqrt{b^2 - 4ac}}{b + \sqrt{b^2 - 4ac}} \right) \quad (3.67)$$

Substituting equation (3.67) in equation (3.65) and after rearrangement, $\theta(\tau, \kappa a_p)$ can be expressed as

$$\theta(\tau, \kappa a_p) = \frac{b - \sqrt{b^2 - 4ac} - \left(b + \sqrt{b^2 - 4ac} \right) \exp \left[\tau \sqrt{b^2 - 4ac} + \ln \left(\frac{b - \sqrt{b^2 - 4ac}}{b + \sqrt{b^2 - 4ac}} \right) \right]}{2a \left\{ \exp \left[\tau \sqrt{b^2 - 4ac} + \ln \left(\frac{b - \sqrt{b^2 - 4ac}}{b + \sqrt{b^2 - 4ac}} \right) \right] - 1 \right\}} \quad (3.68)$$

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In the above equation, the fractional surface coverage is expressed as a function of the dimensionless time and the EDL thickness parameter, κa_p . Hence, the surface coverage can be evaluated analytically for a particular value of κa_p and τ .

3.6 EXPERIMENT

3.6.1 Flow cell design

The experimental system uses a parallel plate flow chamber made of Teflon and glass. Fig 3.4 shows a detailed view of the flow cell design. The top and bottom pieces of Teflon are screwed together where the parallel plate glass channel glued into the gap provided in the Teflon pieces. The glass channel has 100mm length, 6 mm width and 0.3mm depth, and it permits the colloids to be visualized at the channel inner surface and the bulk suspension with equal contrast. Owing to the small effective volume ($\approx 180 \text{ mm}^3$) of the cell, small amounts of suspension are required to perform the experiment for an extended period of time under various flowing conditions.

Fig 3.4 Design of the Parallel plate flow chamber

3.6.2 Experimental System

A schematic of experimental setup is shown in Fig 3.5. A Leica DMLM microscope with dark field illumination is used to visualize and image the colloidal particles deposited on the walls of the glass microchannel. Monodisperse suspensions of polystyrene latex particles of 0.5 and 1 μm in diameter (DUKE SCIENTIFIC, USA) in *NaCl* electrolyte solutions were used in the experiment. The *pH* of the suspension was assumed to remain constant during the period of experiment. In the present study, a particle concentration of $2 \times 10^{14} / \text{m}^3$ was employed in the experiment. Prior to the experiment, the glass microchannels were cleaned by soaking in Acetone, Sodium Hydroxide and Hydrochloric acid for 20 minutes each followed by rinsing many times with Deionized water. Particle suspensions were homogenized ultrasonically prior to the experiment. A peristaltic pump (MASTERFLEX, USA) was used for pumping the suspension continuously. The flow disturbance was reduced by a flow bunker and the flow rate was continuously monitored by a flow meter. The particle images (shown in Fig 3.6) delivered by the objective lens were captured by a digital camera (Leica DC300), and transferred to a PC for further image analysis. Initially, particle images were taken during an interval of 1min, whereas at the later stages, images at 5min intervals were captured. Particle images were processed and counted for the deposited particle number using software (IMAGEPRO).

Fig 3.5. Schematic of experimental setup.

Fig 3.6. Videomicroscopic image of 0.25 μm polystyrene latex particles captured using 50X objective under the experimental conditions: $C = 0.1M$ and $Re = 30$.

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The experimental particle flux (Sherwood number) can be calculated as

$$\text{Sh}_{\text{exp}} = j_0 \left(\frac{a_p}{D_{\infty} n_{\infty}} \right) \quad (3.69)$$

$$\text{where } j_0 = \left(\frac{dn^*}{dt} \right)_{t=0} \quad (3.70)$$

In the above equation, n^* represents the particle concentration per unit area. Hence j_0 represents the slope of the linear portion of the particle concentration curve obtained from experiment.

3.7 Results and Discussion

In this section, the effects of particle size, electrolyte concentration and flow velocity (Reynolds number) on particle deposition are discussed. The physical and electrochemical properties of *NaCl* electrolyte solution at room temperature ($T = 298\text{K}$) were used for the simulation. The parameters for calculating the van der Waals and EDL forces such as Hamaker constant, zeta potential etc. were selected from (Gu and Li 2000, Hunter et al. 2000, Kang et al. 2000). In the present study, the Hamaker constant for the particle wall and interparticle van der Waals interactions was chosen as $0.91 \times 10^{-20} \text{ J}$ (latex-*NaCl*-glass). Particle and wall zeta potentials corresponding to the electrolyte concentrations considered in this study are shown in Table 3.1. As the *pH* of the suspension was assumed to remain constant during the period of experiment, the particle and the channel wall zeta potentials were also assumed to remain unchanged before and after the experiment.

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NaCl Concentration	Zeta potentials	
	ζ_w	ζ_p
0.1M	-18mV	-14mV
0.01M	-23mV	-20mV
0.001M	-28mV	-24mV

Table 3.1 The zeta potentials of latex particles and glass walls corresponding to various electrolyte (NaCl) concentrations.

NaCl Concentration	Dimensionless parameters		
	DI	Da	τ
0.1M	133.8	0.02	259.4
0.01M	258.7	0.01	82
0.001M	364.4	0.007	25.9

Table 3.2 Values of the dimensionless parameters such as DI, Da etc. used for plotting Figure 3.6.

3.7.1 Interaction energy profiles

Fig 3.7 Dimensionless particle-wall interaction energy profiles corresponding to various electrolyte concentrations. $a_p = 0.25 \mu m$, $A = 0.91 \times 10^{-20} J$.

Fig. 3.7 shows the *DLVO* estimations based on the surface parameters selected in this study, where the dimensionless interaction energy (ϕ/kT) is plotted against the dimensionless particle-wall separation distance. The Adhesion number based on the chosen Hamaker constant $A = 0.91 \times 10^{-20} J$, is 0.38. The values of the dimensionless parameters for calculating EDL interactions are provided in table 3.2. It can be noted that for $C = 0.1M$, the resultant particle-wall interaction energy is attractive due to weak repulsive double layer interactions. These cases are generally referred to as favorable

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deposition, where the total colloidal interaction energy is attractive. In the second and third case, (i.e., for $C = 0.01M$ $C = 0.001M$) a repulsive energy barrier exists in the interaction energy profile in the region $0.02 < H < 0.1$, as the repulsive EDL interactions dominate in this region. This case is referred to as unfavorable deposition (Elimelech et al., 1995), as an approaching particle has to overcome the energy barrier in order to make contact with channel wall.

3.7.2 Effect of electrolyte concentration and flow velocity on particle deposition

Fig 3.8 presents the variation of Sherwood number along the channel length (represented by the dimensionless parameter, $\bar{x}$) corresponding to two different solution concentrations, $C = 0.1M$ and $0.01M$. The flow Reynolds number, $Re = 30$ and particle size, $a_p = 0.25 \mu m$. Electrolyte concentration affects particle deposition significantly, where an increase in Sherwood number is observed with an increase in solution concentration. This can be explained from the energy barrier resulting from EDL interactions between charged particles and surfaces, which is primarily controlled by the chemistry of the solution. For $C = 0.1M$, no energy barrier persists and the resulting particle-wall interactions are attractive whereas for the second case an energy barrier nearly equal to $6kT$ exists in the interaction energy profile. This results in higher surface coverage for the former case. Fig 3.9 shows the variation of Sherwood number for $0.25 \mu m$ particles as a function of the flow Reynolds number. Sherwood number for $Re = 30, 60$ has been plotted where $C = 0.1M$ and $a_p = 0.25 \mu m$. It is observed that, an increase in flow velocity reduces particle deposition. The decrease in particle flux in the present case can be attributed to the fact that, with higher flow velocity, convective particle transport dominate

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the transport due to colloidal and external forces, and the particles are swiped away without contacting the channel wall. Also, the Sherwood number slowly declines along the channel length, the rate of which is reduced slightly at higher Reynolds numbers.

Fig 3.8 Comparison of the numerical predictions of Sherwood number with experimental data for different electrolyte concentrations. Parameters used in theoretical calculations are, $Re = 30$. Theoretical parameters: $A = 0.91 \times 10^{-20} J$, $\bar{\lambda} = 0.1$, $a_p = 0.25 \mu m$.

Fig 3.9 Comparison of the numerical predictions of Sherwood number with experimental data represented as a function of the flow Reynolds number. Parameters used in theoretical calculations are, $C = 0.1M$, $A = 0.91 \times 10^{-20} J$, $\bar{\lambda} = 0.1$, $\zeta_p = -14mV$, $\zeta_w = -18mV$, $a_p = 0.25 \mu m$.

3.7.3 Effect of particle size on deposition

Fig 3.10 Theoretical and experimental Sherwood number for two different particle sizes. Parameters used in theoretical calculations are, $C = 0.1M$, $\zeta_p = -14mV$, $\zeta_w = -18mV$, $Re = 30$. Theoretical parameters: $A = 0.91 \times 10^{-20}J$, $\bar{\lambda} = 0.1$.

The effect of particle size on deposition rate is illustrated in Fig. 3.10. Sherwood number at $C = 0.1M$ and $Re = 30$ for two different particle sizes ($a_p = 0.25\mu m$ and $a_p = 0.5\mu m$) are presented. The numerical predictions are in reasonable agreement with the experiment. It can be noticed that there is a significant increase in surface coverage for smaller particles. Colloidal interactions, which are surface forces, become increasingly important

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with reduction in particle size. Hence, the effect of the surface forces on the particle transport to the surface is stronger for smaller particles. Also, results indicate that the Sherwood number variation along the channel length is more pronounced in the case of larger particles. Also, comparing Fig 3.9 and Fig 3.10, it can be inferred that particle size has a stronger effect on deposition compared to the flow velocity.

3.7.4 Comparison of Blocking function results with Experiment

Fig 3.11 Comparison of particle surface coverage based on RSA Blocking function model with experimental result. $Re = 20$, $C = 0.1M$, $\zeta_p = -14mV$, $\zeta_w = -18mV$ $a_p = 0.25 \mu m$.

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The polynomial expression for the Blocking function (given by equation 3.52) is valid only for negligible flow (Adamczyk et al. 1995). In Fig 3.11, particle surface coverages calculated from the Blocking function is compared with the results from experiments for $Re = 20$, $C = 0.1M$ and $a_p = 0.25 \mu m$. It is clearly noticed that the RSA Blocking function overestimates the surface coverage in this case. Large deviation from experiment is observed, especially at the latter stages of deposition ($\tau > 0.5$). It has to be mentioned here that the blocking process is driven by both the hydrodynamic and electrostatic (interparticle repulsion) effects when strong hydrodynamic interactions are present within the system. This leads to the conclusion that, in the case of flowing dispersions and for high surface coverages ($\theta > 0.2$), RSA method is inadequate to model particle deposition. Further, in the present model, the Brownian motion of the particles was neglected which could also be of significance in particle transport when the particle size is less than $1 \mu m$. Hence, in order to model the kinetic of particle deposition in the case of significant flow and higher surface coverages, alternative methods has to be employed. Motivated by this situation, Chapter 4 is devoted for the study of particle deposition from colloidal suspensions from pressure driven and electrokinetic flows, employing a stochastic modeling technique (Brownian dynamics simulation). This model follows a more comprehensive approach to incorporate the effect colloidal and hydrodynamic interactions on the transport and deposition of particles.

3.8 Summary

The irreversible adsorption of colloidal particles from the pressure driven flow in a parallel-plate microchannel has been investigated in this work. The two dimensional mass transport equation that incorporates colloidal and hydrodynamic interactions is derived and solved numerically using a finite difference method. Videomicroscopic experiments are conducted employing the parallel plate flow technique in order to measure the deposition of monodisperse polystyrene latex particles onto glass collector surface. Steady state deposition particle flux (Sherwood number) calculated from the numerical model are compared with the experiment and a reasonable agreement is found. The electrolyte concentration and flow velocity are found to influence deposition significantly, where particle deposition is increased at higher electrolyte concentrations because of weak EDL interactions. Particle size plays an important role in deposition, and higher Sherwood number is observed as the particle size is reduced. The comparison of particle surface coverage based on RSA Blocking function model with experiment reveals that model predictions are valid only for smaller surface coverages ($\theta < 0.2$) and negligible flow velocities. Hence, in an effort to model particle deposition from flows of hydrodynamically interacting suspensions in the high surface coverage regime, Brownian dynamics simulation technique is employed which is described in detail in Chapter 4.

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**BROWNIAN DYNAMICS SIMULATION AND EXPERIMENTAL
STUDY OF COLLOIDAL PARTICLE DEPOSITION FROM
MICROCHANNEL FLOWS****4.1 Introduction**

This chapter deals with the theoretical study on particle deposition from pressure driven and electrokinetic flows, using the Brownian dynamics simulation technique, and the experimental validation using videomicroscopic particle imaging. In the literature, there is a current lack of information on kinetics of particle deposition from electrokinetic flow in microchannels which is important to the design and analysis of chip based microfluidic systems. Hence, this work is motivated by an interest to achieve a fundamental understanding of the particle behavior in pressure driven and electrokinetic particle flows, which can shed light on the design and analysis of microfluidic systems.

In the present work, an attempt has been made to study the deposition of colloidal particles from pressure driven and electrokinetic flow in microchannels; it may be of interest to the surface fouling of microfluidic devices. A mathematical model based on the Brownian Dynamic Simulation technique is presented to compute the particle trajectories and consequently, the surface coverage. In Brownian dynamics simulation method, the effect of the solvent molecules on the transport of solute particles is represented by a combination of random, hydrodynamic and external force terms through stochastic Langevin equation. The so-called “Blocking effect” that stems from the electrostatic and hydrodynamic interactions between deposited and flowing particles, is taken into consideration in the model development. To validate the presented model, experiments are

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carried out using the parallel-plate flow technique. In addition, the effects of the electrolyte concentration, flow velocity and particle size on the particle surface coverage are studied.

4.2 Theory

A geometrical sketch of the microchannel, flow profiles and the associated coordinate system are shown in Fig 4.1. There are two theoretical approaches of modeling particle deposition on the collector surfaces, the Lagrangian method and the Eulerian method (Adamczyk et al., 1983, Swanton, 1995). In the Eulerian method, particle deposition on the collector surfaces is governed by the convection diffusion equation, which also incorporates the colloidal and external forces. The Lagrangian method determines the trajectory of the particles under the effect of colloidal and external forces, and the governing equation of particle transport is the stochastic Langevin equation, including the particle Brownian motion.

Fig 4.1 Microchannel and the associated coordinate system

Fig 4.2 Forces acting on a moving particle in the vicinity of an attached particle and the channel wall

4.2.1 Langevin Equation

The colloidal particle trajectory is governed by the Langevin equation, described by Ermak and McCammon (1978) for flowing colloidal dispersions,

$$d\mathbf{r}_i = \frac{\mathbf{D}_{ij}(t) \cdot \mathbf{F}_i(t)}{k_B T} \Delta t + \nabla_{r_j} \cdot \mathbf{D}_{ij}(t) \Delta t + U(\mathbf{r}_i) \Delta t + (\Delta \mathbf{r})^B \quad (4.1)$$

where $d\mathbf{r}_i$ is the position vector of the i^{th} particle, $\mathbf{D}_{ij}$ is the second-order mutual diffusivity tensor (due to the presence of the neighboring particles), $\mathbf{U}(\mathbf{r}_i)$ is the flow velocity, $\mathbf{F}_i$ is the total force acting on the particle, $(d\mathbf{r})^B$ is the random Brownian displacement of the particle, Δt is the time step (selected from the Brownian relaxation time of the particle), and $k_B T$ is the thermal energy.

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Hence, the velocity of the i^{th} particle can be expressed as

$$U_p = \frac{\mathbf{D}_{ij}(t) \cdot \mathbf{F}_i(t)}{k_B T} + \nabla_{\mathbf{r}_j} \cdot \mathbf{D}_{ij}(t) + U(\mathbf{r}_i) + \frac{(\Delta \mathbf{r})^B}{\Delta t} \quad (4.2)$$

4.2.2 Hydrodynamic interactions

4.2.2.1 Pressure driven flow

In this study, a 6mm wide and 0.3mm deep microchannel is used in the experiment, and hereby the width to depth ratio of the microchannel is 20; this allows us to assume a fully developed flow between two parallel plates. Thus, the pressure driven and electroosmotic flow profiles in the microchannel are given by the expressions,

$$U_{pdf} = \frac{3}{2} V_m \frac{y}{B} \left(2 - \frac{y}{B} \right) \quad (4.3)$$

where V_m is the average flow velocity and B is the half - channel depth.

4.2.2.2 Electrokinetic flow

The electroosmotic flow profile in the microchannel can be given by the expression,

$$U_{eof} = \frac{\varepsilon_0 \varepsilon_r \zeta_w}{\mu} E \quad (4.4)$$

ε_0 and ε_r are the permittivity of vacuum and relative permittivity of the medium respectively, e is the fundamental electronic charge, ζ_p and ζ_w are the particle and wall surface (zeta) potentials, respectively, and E represents the applied electric field strength. Equation (4.4) represents the plug flow velocity profile of electroosmotic flow.

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The motion of a charged particle in response to the applied electric field is named as electrophoresis. The electrophoretic velocity of the particle in the bulk fluid can be expressed as

$$U_{eps} = \frac{\varepsilon_0 \varepsilon_r f(\kappa a_p) \zeta_p}{\mu} E \quad (4.5)$$

The above expression is independent of particle geometry. In equation (4.5), $f(\kappa a_p)$ represents the Henry's correction function for the electrophoretic retardation of a moving particle, caused due to the ions in the electrical double layer surrounding the particle. An expression for $f(\kappa a_p)$, which is applicable for all ranges of κa_p has been provided by Ohshima (1994),

$$f(\kappa a_p) = \frac{2}{3} \left\{ 1 + \frac{1}{2 \left\{ 1 + \frac{2.5}{\kappa a_p [1 + 2 \exp(-\kappa a_p)]} \right\}^3} \right\} \quad (4.6)$$

Hence, the resultant velocity of the particle, in the absence of hydrodynamic interactions due to the wall and neighboring particles can be written as

$$U_{ekp} = \frac{\varepsilon_0 \varepsilon_r E}{\mu} [f(\kappa a_p) \zeta_p \pm \zeta_w] \quad (4.7)$$

where U_{ekp} represents the resultant particle velocity in electrokinetic transport (particle velocity relative to the liquid). Electroosmotic flow would add to or oppose the electrophoretic motion of the particle, depending on the charge polarity of the particles and the wall.

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4.2.2.3 Hydrodynamic force

In the present study, the hydrodynamic force on the moving particle is calculated explicitly. The total hydrodynamic force on the moving particle is computed based on the superposition of the particle-wall and interparticle hydrodynamic force. However, the consideration of many body hydrodynamic interactions involving the spheres present within the system would mean insurmountable computational effects. Hence, for the calculation of interparticle hydrodynamic interactions, pair wise additivity of interactions has been assumed in the present study.

An analytical expression for the hydrodynamic force on a sphere moving parallel to a wall is presented in Happel and Brenner (1986), computed using the method of reflections,

$$\mathbf{F}_{HW} = \frac{-6\pi\mu a_p \mathbf{U}_p}{\left[1 - \frac{9}{16}\left(\frac{a_p}{l}\right) + \frac{1}{8}\left(\frac{a_p}{l}\right)^3 - \frac{45}{256}\left(\frac{a_p}{l}\right)^4 - \frac{1}{16}\left(\frac{a_p}{l}\right)^5\right]} \quad (4.8)$$

where l is the centre (of the sphere) to wall separation distance. The general expression for the hydrodynamic force for the case of relative motion of two particles (regardless of shape) can be given as (Whittle et al. 2000),

$$\mathbf{F}_{HP} = -\mathbf{R}_{FU} \cdot (\mathbf{U}_p - \mathbf{U}^\infty) \quad (4.9)$$

where $\mathbf{R}_{FU}$ is the second-order hydrodynamic resistance tensor and $\mathbf{U}_p$ and $\mathbf{U}^\infty$ are the generalized particle velocity and ambient flow velocity (evaluated at the particle centers), respectively.

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The generalized expression for $\mathbf{F}_{HP}$ can be written in matrix form as (Kim and Karrila, 1991),

$$\begin{bmatrix} \mathbf{F}_{HP1} \\ \mathbf{F}_{HP2} \\ \mathbf{T}_1 \\ \mathbf{T}_2 \end{bmatrix} = \mu \begin{bmatrix} \mathbf{A}_{11} & \mathbf{A}_{12} & \tilde{\mathbf{B}}_{11} & \tilde{\mathbf{B}}_{12} \\ \mathbf{A}_{21} & \mathbf{A}_{22} & \tilde{\mathbf{B}}_{21} & \tilde{\mathbf{B}}_{22} \\ \mathbf{B}_{11} & \mathbf{B}_{12} & \mathbf{C}_{11} & \mathbf{C}_{12} \\ \mathbf{B}_{21} & \mathbf{B}_{22} & \mathbf{C}_{21} & \mathbf{C}_{22} \end{bmatrix} \begin{bmatrix} \mathbf{U}^\infty(\mathbf{y}_1) - \mathbf{U}_{p1} \\ \mathbf{U}^\infty(\mathbf{y}_2) - \mathbf{U}_{p2} \\ \boldsymbol{\omega}^\infty - \boldsymbol{\omega}_1 \\ \boldsymbol{\omega}^\infty - \boldsymbol{\omega}_2 \end{bmatrix} \quad (4.10)$$

In the above expression, $\mathbf{F}_{HPi}$, $\mathbf{T}_{HPi}$, represent the hydrodynamic forces and torques on the first and second particle respectively. $\mathbf{A}_{ij}$ and $\mathbf{B}_{ij}$ represent hydrodynamic resistance tensors (second order) representing the translational and rotational motion of the particle respectively, and $\mathbf{C}_{ij}$ represents the coupling tensor (second order) (Kim and Karrila, 1991). The matrix on the right hand side of equation (4.10) represents $\mathbf{R}_{FU}$, referred to as the grand resistance matrix (Whittle et al., 2000).

Estimation of the hydrodynamic forces and torques requires the determination of translational and rotational velocities of the particle. However, spherical particles are symmetric and hence particle rotation is less likely to affect the colloidal interactions that are responsible for particle deposition, unlike in the case of spheroidal or ellipsoidal particles, where the interaction energy is dependent on particle rotation. Therefore, in this work, the particle rotational velocities are neglected in estimation of the hydrodynamic force. Employing these simplifications, equation (4.10) can be written as

$$\begin{bmatrix} \mathbf{F}_{HP1} \\ \mathbf{F}_{HP2} \end{bmatrix} = \mu \begin{bmatrix} \mathbf{A}_{11} & \mathbf{A}_{12} \\ \mathbf{A}_{21} & \mathbf{A}_{22} \end{bmatrix} \begin{bmatrix} \mathbf{U}^\infty(\mathbf{y}_1) - \mathbf{U}_{p1} \\ \mathbf{U}^\infty(\mathbf{y}_2) - \mathbf{U}_{p2} \end{bmatrix} \quad (4.11)$$

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In the case of the motion of axisymmetric particles, the tensor A_{ij} in equation (4.11) are expanded as (Kim and Karrila, 1991)

$$A_{ij} = X_{ij}^A \mathbf{n}_i \mathbf{n}_j + Y_{ij}^A (\delta_{ij} - \mathbf{n}_i \mathbf{n}_j) \quad (4.12)$$

where $\mathbf{n}_i$ and $\mathbf{n}_j$ represent the unit vectors along the line of centres of the particles and

δ_{ij} is a second order tensor (Kronecker delta). δ_{ij} is defined as

$$\delta_{ij} = 1 \text{ for } i = j, \quad \delta_{ij} = 0 \text{ for } i \neq j \quad (4.13)$$

In order to compute the tensor components, X_{ij}^A and Y_{ij}^A , the results of Jeffrey and Onishi (1984) computed using multipole expansions (for far-field interactions) and lubrication approximation (for near-field interactions) have been employed. However, the near-field results are valid for $H_j \leq 0.05$ whereas the far-field results hold for $H_j \geq 0.5$ (Whittle et al. 2000). Hence for the intermediate range, $0.05 < H_j < 0.5$, cubic spline interpolation was performed to calculate the resistance tensors. The interpolation was performed on the logarithms of the resistance values, as on this scale, the variation is almost linear.

The total hydrodynamic force on the i^{th} particle can be expressed as

$$\mathbf{F}_{Hx} = \sum_{j=1}^N \mathbf{F}_{HP_j} \cos \theta \cos \varphi + \mathbf{F}_{HW}, \quad \mathbf{F}_{Hy} = \sum_{j=1}^N \mathbf{F}_{HP_j} \sin \theta, \quad \mathbf{F}_{Hz} = \sum_{j=1}^N \mathbf{F}_{HP_j} \cos \theta \sin \varphi \quad (4.14)$$

$$\text{where } \theta = \tan^{-1} \left(dY / \sqrt{dX^2 + dZ^2} \right), \quad \varphi = \tan^{-1} (dZ / dX) \quad (4.15)$$

In the above equations, $\mathbf{F}_{HP_j}$ represents the hydrodynamic force on the i^{th} particle because of the presence of the j^{th} neighboring particle, and N is the number of nearest neighbors to the i^{th} particle. In the present study, a cut off radius equal to 10 times the particle radius is

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employed for the numerical calculations, within which the hydrodynamic interactions would be significant.

4.2.2.4 Mutual diffusivity

In dense suspensions, the diffusivity of a moving particle is affected by the neighboring particles. The concentration of particles near to the channel wall is of significance in particle deposition processes. In the simulation study, the minimum value of particle volume fraction ϕ (ratio of the volume of particles to the volume of simulation cell) of $0.5 \mu\text{m}$ particles based on the interparticle separation in the simulation box was found to be 0.05 after the equilibrium step (described in Section 4.3) that ensures steady values of potential energy of the system. Watzlawek and Nagele (1997) have provided an algebraic relation for the ratio of the particle diffusivity to the self diffusivity (estimated from the Stokes-Einstein equation) as a function of particle volume ratio. Using this relation, it can be calculated that the diffusivity ratio for $\phi = 0.05$ is nearly 0.95. This indicates that the particle diffusivity deviates from the self diffusivity at this volume fraction, and the modified diffusivity of a particle due to the presence of neighboring particles (also named as mutual diffusivity) can be expressed as (Elimelech et al., 1995),

$$\mathbf{D}_{ij} = D_i \mathbf{I} + kT \sum_{j=1}^N \mathbf{M}_{ij} \quad (4.16)$$

where D_i is the self-diffusivity of the i^{th} particle defined by the expression $D_i = kT / 6\pi\mu a_p$, $\mathbf{I}$ is the second-order unit tensor, and $\mathbf{M}_{ij}$ is the second-order hydrodynamic mobility tensor that accounts for the interparticle hydrodynamic interactions. The complex tensor expression for $\mathbf{M}_{ij}$ is provided in Appendix 1. Hence,

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equation (4.12) is based on the superposition of hydrodynamic interactions of the neighboring particles on the i^{th} particle.

4.2.3 Colloidal and External Forces

The colloidal transport to the channel wall is affected by various surface and body forces. In the present work, colloidal forces, which are constituted of by the van der Waals and the electric double layer (EDL) forces, and external force such as gravity are taken into consideration. For particle deposition, the EDL force can be either positive or negative, depending on the nature of the charges of the particle and the wall, while the van der Waals force is always attractive. The schematic of various forces acting on a moving particle in the vicinity of another particle and the channel wall is shown in Fig. 4.2.

The total force on the i^{th} particle, F_i is comprised of

$$F_i = F_H + F_{VDW} + F_{EDL} + F_G \quad (4.17)$$

where F_{VDW} , F_{EDL} and F_G represent the Van-der-Waals, EDL and gravity forces, respectively.

The colloidal forces are constituted of both the particle-wall and the interparticle forces. In the present study, interparticle *DLVO* forces are expressed using the superposition rule. This means that the effect of each nearest neighbor particles to the i^{th} particle is superimposed on the particle-wall *DLVO* force to obtain the total *DLVO* force.

The Van der Waals force on the i^{th} particle is given by Adamczyk (1995),

$$F_{VDW} = \frac{-A\lambda a_p(\lambda + 22.22h)}{6h^2(\lambda + 11.11h)^2} \hat{e}_y + \sum_{j=1}^N \frac{-A_j\lambda a_p(\lambda + 22.22h_j)}{12h_j^2(\lambda + 11.11h_j)^2} \hat{e}_{ij} \quad (4.18)$$

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$\hat{e}_y$ is the unit vector in perpendicular to the channel wall, $\hat{e}_{ij}$ is the unit vector in the direction of the mutual separation between particles, h and h_j are the particle-wall separation and the interparticle separation, respectively, A and A_j are the Hamaker constant for the particle-wall and the mutual interaction between particles, respectively, and λ is the London retardation wavelength. In the simulation, N is determined by providing a cut off radius equal to 1.5 times of the particle radius within which the colloidal interactions would be significant (Hutter, 1999).

Similarly, the EDL force on the i^{th} particle is given by (Elimelech et al., 1995),

$$F_{EDL} = \left\{ \begin{aligned} &2\pi\epsilon\kappa a_p \zeta_p \zeta_w \left\{ \frac{2\exp(-\kappa h)}{[1-\exp(-2\kappa h)]} - \frac{(\zeta_p^2 + \zeta_w^2)}{2\zeta_p \zeta_w} \frac{\exp(-2\kappa h)}{[1-\exp(-2\kappa h)]} \right\} \hat{e}_y \\ &+ \sum_{j=1}^N \pi\kappa\epsilon a_p \zeta_p^2 \left\{ \frac{2\exp(-\kappa h_j)}{[1-\exp(-2\kappa h_j)]} - \frac{(\zeta_p^2 + \zeta_w^2)}{2\zeta_p \zeta_w} \frac{\exp(-2\kappa h_j)}{[1-\exp(-2\kappa h_j)]} \right\} \hat{e}_{ij} \end{aligned} \right\} \quad (4.19)$$

The gravity force is expressed as

$$F_G = -\frac{4}{3}\pi a_p^3 (\rho_p - \rho_f) g \hat{e}_y \quad (4.20)$$

where ρ_p and ρ_f are the particle and fluid densities, respectively.

4.2.4 Brownian Motion

The random Brownian displacement of a particle (due to collisions with the fluid molecules) is represented by a Gaussian distribution with zero mean and variance depending on the mutual diffusivity of the particles.

$$\langle \Delta \mathbf{r}^B \Delta \mathbf{r}^B \rangle = 2\mathbf{D}_{ij} \Delta t \quad (4.21)$$

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where D_{ij} is the mutual diffusivity of the i^{th} particle and Δt is the simulation time step, determined from the Brownian relaxation time of the particle, τ_{Br} (Hutter, 1999),

$$\tau_{Br} = \frac{a_p^2}{6D_i} \quad (4.22)$$

The time step for simulation should be chosen to be sufficiently smaller than the Brownian relaxation time of the particle (Hutter, 1999). In the present study, a time step of $3 \times 10^{-5} \tau_{Br}$ was selected and the total number of time steps corresponding to the total simulation time (t) were 2×10^8 and 2.5×10^7 , respectively for $0.25 \mu\text{m}$ and $0.5 \mu\text{m}$ particles.

4.3 SIMULATION

The particle transport was simulated in a cubic simulation cell containing arbitrary number of particles, 27, 64, 125, 216 etc. Computational tests were performed to determine the optimum number of particles (N_p), above which, the variation in surface coverage is negligible. Periodic boundary conditions are applied on all the faces of the cell to eliminate the surface effects associated with the finite size of the cell (Adamczyk et al 1995). This means that the simulation cell is replicated as an infinite lattice and as the particle leaves through one face of the cell, an image of the particle enters through the opposite face. The particle positions were computed according to equation (4.1) using a modified Euler approach, i.e., the predicted (superscript p) particle position is calculated from equation (4.1) from the current position and the parameters of Langevin equation are determined at this position. The mean of the parameters at the current and the predicted positions is then used to compute the corrected (superscript c) particle position from the

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predicted positions. The position of a particle i at time $(t + \Delta t)$ is computed based on the position of $(N-1)$ particles at time t . Once steady values over time for the potential energy of the system are achieved, the resulting particle configurations are selected as the starting configurations for the simulation (Equilibrium step). The particle is assumed to be adsorbed on the surface once the primary energy minimum separation, H_0 is reached. H_0 is the closest separation distance (dimensionless) between the particle and the wall. In the simulation study, computational tests were performed to estimate the influence of the choice of H_0 on the surface coverage. It was found that the results are insensitive to the choice of H_0 as long as $H_0 \leq 0.002$. This means that a change in the value of H_0 by 5×10^{-4} causes a change in the calculated surface coverage by 0.1%. Hence, $H_0 = 0.002$ was used for all the simulation runs. The details of this algorithm are outlined in the following equations.

$$\mathbf{r}_{i+\Delta t}^p = \mathbf{r}_i + (d\mathbf{r})_i^p \quad (4.23)$$

$$(d\mathbf{r})_i^p = \sum_j \frac{\mathbf{D}_{ij}(\mathbf{r}_i) \cdot \mathbf{F}_j(\mathbf{r}_i)}{kT} \Delta t + \nabla_{r_j} \cdot \mathbf{D}_{ij}(\mathbf{r}_i) \Delta t + U(\mathbf{r}_i) \Delta t + (\Delta \mathbf{r})^B \quad (4.24)$$

$$(d\mathbf{r})_i^c = \sum_j \frac{[\mathbf{D}_{ij}(\mathbf{r}_i) + \mathbf{D}_{ij}(\mathbf{r}_{i+\Delta t})^p] \cdot [\mathbf{F}_j(\mathbf{r}_i) + \mathbf{F}_j(\mathbf{r}_{i+\Delta t})^p]}{4kT} \Delta t + \frac{1}{2} [\nabla_{r_j} \cdot \mathbf{D}_{ij}(\mathbf{r}_i) + \nabla_{r_j} \cdot \mathbf{D}_{ij}(\mathbf{r}_{i+\Delta t})^p] \Delta t + \frac{[U(\mathbf{r}_i) + U(\mathbf{r}_{i+\Delta t})^p]}{2} \Delta t + (\Delta \mathbf{r})^B \quad (4.25)$$

$$\mathbf{r}_{i+\Delta t}^c = \mathbf{r}_i + (d\mathbf{r})_i^c \quad (4.26)$$

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Based on the simulation results, the particle surface coverage is calculated using the expression,

$$\theta = \frac{\pi a_p^2 N_d}{\Delta S} \quad (4.27)$$

where N_d is the number of deposited particles, and ΔS is the surface area of the simulation cell.

4.4 EXPERIMENT

4.4.1 Electrokinetic Flow cell Design

To validate the Brownian dynamics simulation results, particle deposition experiments were carried out using the parallel-plate flow technique. In Chapter 3, the flow cell design and the arrangement for pressure driven flow experiments was elaborated. Fig 4.3 shows the design of the electrokinetic flow cell employed for particle deposition experiments. It consists of a glass microchannel in connection with two Teflon blocks that are machined to form the reservoirs (marked as **R1** and **R2** in Fig 4.3). The dimensions of the reservoir chamber are so selected as to keep the reservoir level difference at a minimum value, less than 2 %, after continued flow of the suspension for 90 minutes through the microchannel. These blocks are covered on top by rubber gaskets. Platinum electrodes of thickness 0.2mm are inserted in both the reservoirs. The parallel plate glass channel has 100mm length, 6 mm width and 0.3mm depth, and it permits the colloids to be visualized at the channel inner surface and the bulk suspension with equal contrast. Owing to the small effective volume (180 mm³) of the cell, small amounts of suspension are required to perform the experiment for an extended period of time under various flowing conditions.

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Fig. 4.3 Electrokinetic flow cell design

4.4.2 Experimental System

Fig 4.4. Schematic of experimental setup for electrokinetic flow experiment

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A schematic of experimental setup is shown in Fig 4.4. A Leica DMLM microscope with dark field illumination is used to visualize and image the colloidal particles deposited on the walls of the glass microchannel. Monodisperse suspensions of polystyrene latex particles of 0.5, 1 and 2.9 μm in diameter (DUKE SCIENTIFIC, USA) in NaCl electrolyte solutions were used in the experiment. The pH of the suspension was assumed to remain constant during the period of experiment. Prior to the experiment, the glass microchannels were cleaned by soaking in Acetone, Sodium Hydroxide and Hydrochloric acid for 20 minutes each followed by rinsing many times with Deionized water. Particle suspensions were homogenized ultrasonically prior to the experiment. The platinum electrodes were connected to a constant DC power source (STANFORD INSTRUMENTS, USA) which provides uninterrupted power supply during the course of the experiment. The particle images delivered by the objective lens were captured by a digital camera (Leica DC300), and transferred to a PC for further image analysis. Initially, particle images were taken during an interval of 1min, whereas at the later stages, images at 5min intervals were captured. Particle images were processed and counted for the deposited particle number (N_c) using software (IMAGEPRO).

The particle surface coverage based on experimental data is determined as

$$\theta = \frac{\pi a_p^2 N_c}{\Delta A} \quad (4.24)$$

where N_c is the deposited particle number and ΔA is the view area of particle deposition experiment.

4.5. RESULTS AND DISCUSSION

In this section, the effects of particle size, electrolyte concentration and flow velocity (Reynolds number) on the particle surface coverage are discussed. The physical and electrochemical properties of *NaCl* electrolyte solution at room temperature ($T = 298\text{K}$) were used for the simulation. The details regarding the Van der Waals and EDL parameter selection were discussed in Chapter 3. In the present study, Hamaker constants for the particle wall and interparticle van der Waals interactions were chosen as $0.91 \times 10^{-20} \text{ J}$ (latex-*NaCl*-glass) and $0.38 \times 10^{-20} \text{ J}$ (latex-*NaCl*-latex), respectively (Particle and wall zeta potentials corresponding to the electrolyte concentrations considered in this study are shown in Table 3.1). As the *pH* of the suspension was assumed to remain constant during the period of experiment, the particle and the channel wall zeta potentials were also assumed to remain unchanged before and after the experiment.

4.5.1 Particle number independency test

Fig. 4.5 shows the surface coverages computed with different particle numbers (N_p) for Reynolds number $Re = 30$, electrolyte concentration $C = 0.01\text{M}$ and particle radius $a_p = 0.25\mu\text{m}$ as a function of time. The computation was performed to ensure that the simulation results are independent of the choice of the particle number. Simulations were carried out using $N_p = 27, 64, 125$ and 216 . The results corresponding to $N_p = 27$ show a noticeable difference from the results of other three particle numbers. It was found that the use of the particle number $N_p \geq 125$ could produce particle number independent results and hence $N_p = 125$ was used for all simulation runs.

Fig 4.5 Surface coverages versus time computed using different particle numbers. Other parameters used in simulation are $a_p = 0.25 \mu m$, $Re = 30$, $C = 0.01M$, $\zeta_w = -23mV$, $\zeta_p = -20mV$, $A = 0.91 \times 10^{-20} J$, $A_j = 0.38 \times 10^{-20} J$, and $\rho = 1050 kg/m^3$.

4.5.2 Simulation results for pressure driven flow

4.5.2.1 Effect of Electrolyte concentration

The effect of electrolyte concentration on particle deposition is presented in Fig 4.6. Surface coverages of $0.25 \mu m$ particles at $C = 0.1M$, $0.001M$ and $Re = 30$ are plotted. The solid lines represent the simulations results whereas the symbols denote the experimental data.

Fig 4.6 Deposition kinetics of 0.25 μm particles at different electrolyte concentrations. Other parameters used in simulation are $\text{Re} = 30$, $A = 0.91 \times 10^{-20} \text{ J}$, $A_j = 0.38 \times 10^{-20} \text{ J}$, and $\rho = 1050 \text{ kg/m}^3$.

Fig 4.7. Deposition kinetics at different electrolyte concentrations as a function of flow Reynolds number. Other parameters used in simulation are $\tau = 1$, $a_p = 0.25\mu m$, $A = 0.91 \times 10^{-20} J$, $A_j = 0.38 \times 10^{-20} J$, and $\rho = 1050 kg/m^3$.

As is evident from the figure, the surface coverage is larger for higher electrolyte concentrations. This can be attributed to the repulsive double layer interactions between the same charge polarity (negative) of the latex particles and glass wall. A linear adsorption regime is observed at the initial stages, after which, a tendency for saturation is noted. Similar kinetic saturations of the interfaces were observed by Adamczyk (1995)

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and Yang et al. (1999) in deposition experiments using the impinging jet and parallel-plate channel flow techniques. The reduction in particle deposition at the later stages can be explained by taking into account the surface blocking which is dependent on the combined effect of Hydrodynamic (particle velocity) and EDL interactions. The electrical and hydrodynamic interactions between the deposited and flowing particles causes the displacement of an approaching particle away from the channel wall, hence, preventing deposition. The double layer interactions are dependent on electrolyte concentration and are reduced at higher electrolyte concentrations. Fig 4.7 shows the variation of surface coverages with the Reynolds number corresponding to $\tau = 1$ for three different electrolyte concentrations. For the range of concentrations studied, the deposition rate decreases significantly with an increase in the Reynolds number. The effect of the Reynolds number is more pronounced at $C = 0.1\text{M}$ than at the two lower concentrations. This is due to the stronger Blocking effect resulted from more deposited particles. Further, the simulation results are found to be in quantitative agreement with the experimental results.

4.5.2.2 Effect of hydrodynamic flow

The effect of the Reynolds number on the surface coverage is presented in Fig 4.8. Surface coverages of $0.25\mu\text{m}$ particles corresponding to $\text{Re} = 30$ and $\text{Re} = 60$ at $C = 0.1\text{M}$ are plotted. The flow Reynolds number is defined as $\text{Re} = \frac{2V(2B)}{\nu}$, where V is the average fluid velocity; $2B$ is the depth of the microchannel (in the case of parallel plate channels, the hydraulic diameter, $D_h = 2 \times \text{depth of the channel}$) and ν is the kinematic viscosity of fluid.

Fig 4.8. Deposition kinetics of $0.25 \mu\text{m}$ particles at different Reynolds numbers. Other parameters used in simulation are $C = 0.1\text{M}$, $\zeta_w = -18\text{mV}$, $\zeta_p = -14\text{mV}$, $A = 0.91 \times 10^{-20} \text{ J}$, $A_j = 0.38 \times 10^{-20} \text{ J}$, and $\rho = 1050 \text{ kg/m}^3$.

It can be observed that an increase in the flow intensity decreases the deposition rate significantly. One can observe from Fig. 8 that the slope of the curve for $Re = 60$ is much less than that for $Re = 30$, particularly at the late stages of deposition. This shows that when $\tau > 0.5$, the flow conditions strongly influence deposition, leading to saturation of the surface. This indicates a stronger blocking effect is present in the latter case due to the presence of increasing importance of hydrodynamic interactions. Hence, most of the particles are transported without being able to contact the wall. Adamczyk et al. (1995)

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however has observed an increase in surface coverage at higher Reynolds numbers in impinging jet flows. This can be attributed to the fact that flow velocity facilitates the deposition in the impinging jet cell flows; whereas in the parallel plate channel geometry, the flow swipes particles away from the channel wall.

Fig 4.9 Testing of the limitation of the RSA Blocking function approach at high Re. $C = 0.1M$.

Figure 4.9 shows the comparison of the analytical Blocking function given by equation (3.68) and the experimental surface coverages at $Re = 20$ and $Re = 30$ for $C = 0.1M$, in order to judge the limitation of Blocking function. It can be clearly noticed that the RSA

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Blocking function fails to predict the kinetics of deposition especially at $Re = 30$ whereas some initial agreement is observed for $Re = 20$.

4.5.2.3 Effect of particle size

The effect of particle size on deposition rate is illustrated in Fig. 4.10 and Fig. 4.11. Surface coverages at $C = 0.1M$ and $Re = 30$ for two different particle sizes ($a_p = 0.25\mu m$ and $a_p = 0.5\mu m$) are presented in Fig.4.10. A significant increase in surface coverage for smaller particles can be observed. This can be explained in light of the fact that the colloidal interactions, which are surface forces, become increasingly important with reduction in particle size. Hence, the effect of the surface forces on the particle transport to the surface is stronger for smaller particles. Furthermore, since the area occupied by the deposited particles is expressed as $\pi a_p^2 N_d$, being proportional to the square of particle radius, the available surface area for particle deposition is reduced for large particles. As a result, further deposition of $0.5\mu m$ particles is prevented due to stronger Blocking effects. Hence, there is no significant increase in deposition for $0.5\mu m$ particles at the late stages of deposition compared to $0.25\mu m$ particles. The simulation results are in good agreement with the experimental data, indicating that the two-body superposition approach employed in the computation of interparticle forces is a good approximation when dealing with dilute suspensions.

Fig 4.10. Deposition kinetics for different particle sizes. Other parameters used in simulation are $Re = 30$, $C = 0.1M$, $\zeta_w = -18mV$, $\zeta_p = -14mV$, $A = 0.91 \times 10^{-20} J$, $A_j = 0.38 \times 10^{-20} J$, and $\rho = 1050 kg/m^3$.

Fig 4.11. Effect of particle size on particle deposition kinetics. Other parameters used in simulation are $\tau=1$, $C = 0.1M$, $\zeta_w = -18mV$, $\zeta_p = -14mV$, $A = 0.91 \times 10^{-20} J$, $A_j = 0.38 \times 10^{-20} J$, and $\rho = 1050 kg/m^3$.

Fig. 4.11 shows the variation of surface coverage with the Reynolds number corresponding to two different particle sizes for $C = 0.1M$ and $\tau = 1$. At higher flow intensities, the convection effects circumvent the effect due to colloidal forces and the particles are transported in the microchannel without being deposited. The difference in surface coverage for particle sizes $0.25 \mu m$ and $0.5 \mu m$ decreases with increase in the

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Reynolds number. This is indicated by the higher slope of the curve corresponding to $a_p = 0.25 \mu\text{m}$.

4.5.3 Simulation results for Electrokinetic flow

4.5.3.1 Effect of Electric field strength

Fig 4.12. Deposition kinetics of $0.25 \mu\text{m}$ particles in electrokinetic flow for different Electric field strengths. Other parameters used in simulation are $C = 0.01\text{M}$, $\zeta_w = -23\text{mV}$, $\zeta_p = -20\text{mV}$, $A = 0.91 \times 10^{-20} \text{ J}$, $A_j = 0.38 \times 10^{-20} \text{ J}$, and $\rho = 1050 \text{ kg/m}^3$.

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Fig 4.12 shows the effect of electric field strength on particle deposition in the parallel plate microchannel. Surface coverages of $0.25\mu\text{m}$ particles are plotted for two electric field strengths, $E = 5 \times 10^3 \text{ V/m}$ and $E = 10^4 \text{ V/m}$, where the solution concentration $C = 0.01\text{M}$. The applied field strength is observed to influence deposition strongly, where a marked difference can be noticed in the surface converges. The particle velocity is dependent of the applied field strength, and hence, in the case of high field strengths, the particles are swiped away without contacting the wall. Another interesting point is that the Reynolds number based on the fluid flow velocity (electroosmotic flow velocity) and channel characteristic length ($4B$) in the case of $C = 0.01\text{M}$ ($\zeta_w = -23\text{mV}$, $\zeta_p = -20\text{mV}$) and $E = 10^4 \text{ V/m}$ is nearly equal to 0.1. Furthermore, as the particles and channel wall are of the same polarity in the present case, the electroosmotic flow opposes the particle velocity due to electrophoresis. Hence, the particle velocity is significantly small compared to the case of pressure driven flow, even at moderate field strengths. It can be observed that there is a significant difference in the rates of kinetic saturation of the collector surface corresponding to $E = 5 \times 10^3 \text{ V/m}$ and $E = 10^4 \text{ V/m}$. This implies that the surface blocking is mostly contributed by electrical interactions between particles since the hydrodynamic blocking is relatively weaker, owing to the small flow velocity. Hence, a faster kinetic saturation of the surface can be observed in the curve corresponding to the smaller field strength caused due to the increased electrical interactions resulted from more deposited particles.

4.5.3.2 Effect of particle size

Fig 4.13. Deposition kinetics in electrokinetic flow for different particle sizes. Other parameters used in simulation are $E = 5 \times 10^3 V/m$, $C = 0.01M$, $\zeta_w = -23mV$, $\zeta_p = -20mV$, $A = 0.91 \times 10^{-20} J$, $A_j = 0.38 \times 10^{-20} J$, and $\rho = 1050 kg/m^3$.

Fig 4.13 represents the surface coverages corresponding to various particle sizes ($0.25\mu m$, $0.5\mu m$, and $1.45\mu m$) for $C = 0.01M$ and $E = 5 \times 10^3 V/m$. The simulation results are found to be in reasonable agreement with experiment. It can be observed that a faster kinetic saturation is achieved in the case of larger particles ($1.45\mu m$), whereas for smaller particles ($0.5\mu m$ and $1\mu m$) deposition tend to saturate relatively slower rate. It has to be mentioned here that, in the case of $a_p = 1.45\mu m$, the area covered by the one deposited

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particle is nearly 9 times the area covered by a $0.5\mu\text{m}$ particle. This results in a reduction in the available surface area for particle deposition and stronger blocking in the previous case, thereby achieving surface saturation at a faster rate.

4.5.3.3 Comparison of particle surface coverage in pressure driven and eletrokinetic flows based on the same flow Reynolds number

Fig 4.14. Deposition kinetics in pressure driven and electrokinetic flows compared based on the same flow Reynolds number ($\text{Re} = 5$). Other parameters used in simulation are $E = 5 \times 10^3 \text{ V/m}$, $C = 0.001 \text{ M}$, $\zeta_w = -28 \text{ mV}$, $\zeta_p = -24 \text{ mV}$, $A = 0.91 \times 10^{-20} \text{ J}$, $A_j = 0.38 \times 10^{-20} \text{ J}$, and $\rho = 1050 \text{ kg/m}^3$.

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Fig 4.14 shows the comparison of the simulation results for pressure driven and electrokinetic flow which is based on $Re = 5$. The flow Reynolds number in electrokinetic flow is defined as $Re = \frac{2U_s(2B)}{\nu}$, where $2B$ is the channel depth, and U_s is the Smoluchowski velocity of the electrolyte solution (represented by equation 4.4). With the solution concentration $C = 0.001M$ ($\zeta_w = -28mV$), the electric field strength in this case, $E = 4.2 \times 10^5 V/m$. An increase in deposition is observed in the case of electrokinetic flow, especially in the initial stages of deposition. At the later stages ($\tau > 0.5$), particle deposition tend to saturate at a faster rate compared to pressure driven flow. It has to be noted that, in the present case, with the particles and wall having similar charge polarity, the electrophoretic motion of the particle and the electroosmotic flow of the fluid counteract each other, and the velocity of a moving particle is considerably reduced. These conditions strongly influence deposition, and a higher surface coverage is resulted in the case of electrokinetic flow. However, at the later stages, the Blocking effect due to the adsorbed particles becomes predominant and a faster kinetic saturation of the surface is achieved.

4.5.4 Comparison of theoretical predictions with experimental results

In the present study, a good agreement exists between theory and experiment for the range of electrolyte concentrations and flow Reynolds numbers studied. There are two cases in particle deposition studies that should be mentioned in this regard; (i) favorable deposition where the combined van der Waals and EDL interactions between the particle and wall are attractive, (ii) unfavorable deposition where a repulsive energy barrier exists in the interaction energy profile. In the literature, good agreement between theory and

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experiment has been reported when deposition occurred under favorable conditions (Adamczyk et al. (1995), Elimelech et al. (1991)). In contrast, large discrepancies are usually found between theoretical and experimental deposition rates under unfavorable deposition conditions (Sjollema and Buscher 1989, Elimelech and O’Meila 1990). The reasons for these discrepancies are attributed to various stochastic effects such as particle and wall surface roughness, surface charge heterogeneity and nonuniformity in the particle and wall surface (zeta) potential etc.

Fig 4.15. Dimensionless particle-wall interaction energy profile for $C = 0.01M$ and $a_p = 1.45 \mu m$, $A = 0.91 \times 10^{-20} J$.

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In the previous chapter, Fig 3.6 shows the DLVO estimations based on the surface parameters selected in this study, where the dimensionless interaction energy (ϕ / kT) for $0.25 \mu m$ particles is plotted against the dimensionless particle-wall separation distance. It can be noted that for $C = 0.1M$, the resultant particle-wall interaction energy is attractive due to weak repulsive double layer interactions. Hence the agreement between theory and experiment for the two lower concentrations is not surprising given that the deposition occurred under such favorable conditions. However, when $C = 0.01M$ and $C = 0.001M$, a repulsive energy barrier of $6kT$ and $16.9kT$ are present respectively, and thus the deposition can be considered under an unfavorable condition. However, as the energy barrier can not be considered high (Elimelech et al. 1995), any mechanisms such as Brownian motion which have not been included in conventional models may be responsible for the occurrence of particle deposition. Figure 4.15 above shows the interaction energy profile, calculated for $a_p = 1.45 \mu m$ and $C = 0.01M$. The above figure shows that a minimum of $-2kT$ exists in the energy profile after the energy barrier, which is termed as the “secondary minimum”. This also can affect particle deposition due to the formation of weak aggregates in the case of larger particles. Also, from an experimental viewpoint, the disturbances due to hydrodynamic flow and interaction, surface interaction forces, and Brownian effect would possibly cause particles to overcome such a small energy barrier and thus to achieve deposition. In addition, it should be pointed out here the surface properties of the particles and wall (zeta potentials and Hamaker constant) were not directly measured in the experiment and instead they were selected from the literature. The differences between the selected and the true values of the surface properties can cause variations in the height of the energy barrier, resulting in particle deposition.

4.6 SUMMARY

The irreversible adsorption of colloidal particles from the pressure driven flow in a parallel-plate microchannel has been investigated in this work. The Brownian dynamics simulation technique based on the stochastic Langevin equation was employed for computation of particle surface coverage. Deposition experiments using the parallel-flow technique were carried out to compare the simulation results, and a good agreement was found for the range of Reynolds numbers studied. Further, the electrolyte concentration was found to influence the surface coverage significantly at lower Reynolds numbers; however such effect is reduced at higher Reynolds numbers due to the increased particle velocity and scattering of the moving particles in the vicinity of the deposited particles. In addition, as the particle size is reduced, the particle deposition increases due to increasing contributions of the colloidal interaction forces. Again, the effect of particle size starts decreasing at high Reynolds numbers. Pressure driven and electrokinetic flows are compared based on the same flow Reynolds number, and it is found that higher particle deposition is observed in electrokinetic flows, when the particles and the channel wall have the same charge polarity.

CHAPTER 5

ELECTROKINETIC TRANSPORT OF TWO SPHERES IN A PARALLEL PLATE MICROCHANNEL

5.1 Introduction

Chip based microfluidic devices that are used for biological cell/particle manipulation (e.g. cell sorting, separation) involve electrokinetic transport of these particles in microchannels whose size is comparable with the particle size. The cells are a few microns in diameter (for e.g. in Blood, the Red blood cell (RBC) is of $(7-10) \mu m$ in size, White blood cell (WBC) is of $(10-15) \mu m$ in size and the platelets are $(2-4) \mu m$ in size) and therefore, in the modeling of cell transport in microchannels of comparable size necessitates the consideration of boundary effects. In such cases, the applied electric field and the flow field would be influenced by the particles and the channel walls; it would be interesting to know how these perturbations affect the particle velocities, and in turn, particle trajectories. The present work makes an analytical study on the electrokinetic transport of two spherical particles in a parallel plate microchannel with reference to the planar motion of spheres, in an effort to understand the effect of particle size, electric field strength, zeta potential etc. on the particle transport. The wall disturbances are represented by complex Fourier transforms whereas spherical harmonics functions represent the disturbance due to the presence of the spheres. The Fourier transform of the wall disturbance is analytically inverted to satisfy the boundary conditions on the surface of the spheres. The resulting unknown harmonic functions are computed by using the boundary collocation method; i.e., by truncating the infinite spherical harmonic series and

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applying the boundary conditions on finite points on the surface of the spheres, yielding a set of simultaneous equations that can be solved by matrix reduction.

The analysis of the results is made into three parts. Firstly, the symmetric and asymmetric motion of a sphere in a microchannel is explained and the effect of the relative particle size and eccentricity of particle motion on the particle velocities are discussed. The following part deals with the electrokinetic transport of a sphere in the vicinity of an attached sphere in a microchannel. The last section deals with the planar electrokinetic transport of two moving spheres in a microchannel. The effects of relative particle size, applied field strength, particle zeta potential, interparticle or particle-wall separation on the particle velocities and trajectories are discussed in detail.

5.2 Problem Domain

Fig 5.1 Geometrical sketch of two particle - electrophoresis in a microchannel

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In the present study, the planar electrokinetic motion of colloidal particles in a parallel plate microchannel is considered. Fig 5.1 shows the geometrical sketch of electrokinetic transport of two spheres in a parallel plate microchannel. Here, (r_i, θ_i, ϕ_i) represent the spherical coordinate systems originating from the centre of each sphere and (x, y, z) represent Cartesian coordinate system that is fixed on one of the spheres. The uniformly applied electric field is represented by $E_x \mathbf{e}_x$, where $\mathbf{e}_x$ represents the unit vector in the X direction. The thicknesses of the electrical double layers adjacent to the solid surfaces is assumed to be small relative to the radius of the spheres and the surface to surface spacing ratio between the particles and the wall. Also, gravitational effects are neglected in the present study. The objective is to determine the velocity and trajectory of the particles, for which the electrical potential and velocity fields in the fluid phase must be solved.

5.3 Electrical potential distribution

5.3.1 Governing equations and boundary conditions

The fluid outside the thin double layers is assumed to be electrically neutral as is assumed to be of constant conductivity; hence the electrical potential distribution in the fluid is governed by the Laplace equation,

$$\nabla^2 \phi = 0 \quad (5.1)$$

The potential gradient far from the particle approaches the undisturbed applied electric field and the normal component of the current flux at the surface of the insulating particles and channel walls vanishes. Thus, the electrical potential in the fluid is subjected to the following boundary conditions,

$$\mathbf{e}_z \cdot \nabla \phi = 0 \quad \text{at } z = c, z = -b \quad (5.2a)$$

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$$e_{r_j} \cdot \nabla \phi = 0 \quad \text{at } r_j = a_j \quad (5.2b)$$

Since the governing equations and boundary conditions are linear, the total electrical potential in the fluid, ϕ can be expressed as a superposition,

$$\phi = \phi_w + \phi_s - E_\infty x \quad (5.3)$$

In the above equation, E_∞ represents the applied electric field strength. ϕ_w represents the disturbance to the applied electric field caused by the two plane walls and can be represented by a general Fourier integral solution to Laplace equation in Cartesian coordinates (Keh et al. 2002),

$$\frac{\partial^2 \phi}{\partial x^2} + \frac{\partial^2 \phi}{\partial y^2} + \frac{\partial^2 \phi}{\partial z^2} = 0 \quad (5.4)$$

$$\phi_w = E_\infty \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} [X \exp(\kappa z) + Y \exp(-\kappa z)] \exp[i(\alpha x + \beta y)] d\alpha d\beta \quad (5.5)$$

where ϕ_w is the disturbance in electrical potential caused by the walls. α and β are the separation variables and $\kappa = \sqrt{\alpha^2 + \beta^2}$. X and Y are functions of α and β .

In equation (5.3), ϕ_s represents the disturbance to the applied electric field caused by the presence of the spheres. ϕ_s can be expressed as the solution to the Laplace equation in spherical coordinates,

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \phi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \phi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \phi}{\partial \varphi^2} = 0 \quad (5.6)$$

The fundamental solution of the Laplace equation that can describe an arbitrary disturbance caused by the spheres includes the solid spherical harmonic functions. For N spheres dispersed in electrical potential fields, the general solution to equation (5.6) can

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be expressed by a superposition of this fundamental solution in the spherical coordinates originating from the centers of N spheres (Keh et al. (1993)),

$$\phi_s = E_\infty \sum_{j=1}^N \sum_{n=0}^{\infty} \sum_{k=0}^n r_j^{-(n+1)} P_n^k(q_j) [R_{jkn} \cos(k\varphi_j) + S_{jkn} \sin(k\varphi_j)] \quad (5.7)$$

In the above equation, ϕ_s represents the disturbance caused by the spheres. r_j represents the radial coordinate from the center of the j^{th} sphere, $P_n^k(q_j)$ is the associated Legendre polynomial of the first kind having order n and degree k ($q_j = \cos\theta_j$ where θ_j is the polar angle corresponding to the j^{th} sphere) and φ_j represents the azimuthal angle corresponding to the j^{th} sphere.

5.3.2 Analytical Modeling using Fourier integral – Hankel transform approach

Using equation (5.3), the total electrical potential in the fluid, ϕ for the case of the motion of two spheres (represented by 1 and 2 in Fig 5.1) in a parallel plate microchannel can be expressed as

$$\phi = E_\infty \left[\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} (Xe^{\kappa z} + Ye^{-\kappa z}) \exp[i(\alpha x + \beta y)] d\alpha d\beta - x + \sum_{j=1}^2 \sum_{n=0}^{\infty} \sum_{k=0}^n r_j^{-(n+1)} P_n^k(q_j) [R_{jkn} \cos(k\varphi_j) + S_{jkn} \sin(k\varphi_j)] \right] \quad (5.8)$$

Substituting equation (5.7) into equation (5.2a) yields

$$\frac{\partial \phi}{\partial z} = E_\infty \left\{ \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \kappa [X \exp(\kappa z) - Y \exp(-\kappa z)] \exp[i(\alpha x + \beta y)] d\alpha d\beta + \frac{\partial}{\partial z} \left\{ \sum_{n=0}^{\infty} \sum_{k=0}^n r_1^{-(n+1)} P_n^k(q_1) [R_{1kn} \cos(k\varphi_1) + S_{1kn} \sin(k\varphi_1)] + \sum_{n=0}^{\infty} \sum_{k=0}^n r_2^{-(n+1)} P_n^k(q_2) [R_{2kn} \cos(k\varphi_2) + S_{2kn} \sin(k\varphi_2)] \right\} \right\} = 0 \quad (5.9)$$

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where $q_1 = \cos(\theta_1)$, $q_2 = \cos(\theta_2)$.

In order to express the electrical potential distribution in terms of a single coordinate system, it is necessary to perform a transformation of the coordinates of a point P in space (as indicated in Fig 5.1) relative to the first and second spheres. The corresponding geometrical relations in space can be expressed as (Hassonjee et al., 1988),

$$r_2 = \sqrt{2r_1(b_{12} \sin \theta_1 \cos \varphi_1 + c_{12} \sin \theta_1 \sin \varphi_1 + d_{12} \cos \theta_1) + r_1^2 + b_{12}^2 + c_{12}^2 + d_{12}^2} \quad (5.10)$$

$$\theta_2 = \tan^{-1} \left[\frac{\sqrt{\{[r_1^2 \sin \theta_1 + b_{12}^2 + c_{12}^2 + 2r_1 \sin \theta_1 (b_{12} \cos \varphi_1 + c_{12} \sin \varphi_1)]\}}}{d_{12} + r_1 \cos \theta_1} \right] \quad (5.11)$$

$$\varphi_2 = \tan^{-1} \left(\frac{r_1 \sin \theta_1 \sin \varphi_1 + c_{12}}{r_1 \sin \theta_1 \cos \varphi_1 + b_{12}} \right) \quad (5.12)$$

where $b_{12} = b_1 - b_2$, $c_{12} = c_1 - c_2$, $d_{12} = d_1 - d_2$. In the present study, the Cartesian coordinate system is fixed on sphere, 1, and hence, $(b_1, c_1, d_1) = 0$.

Hence, $\frac{\partial \phi}{\partial z}$ can be expressed as

$$\frac{\partial \phi}{\partial z} = E_\infty \left\{ \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \kappa [X \exp(\kappa z) - Y \exp(-\kappa z)] \exp[i(\alpha x + \beta y)] d\alpha d\beta \right. \\ \left. \sum_{n=0}^{\infty} \sum_{k=0}^n \left[-z(n+1)r_1^{-(n+3)} P_n^k(q_1) + r_1^{-(n+1)} \frac{\partial P_n^k(q_1)}{\partial z} \right] f_1 \right. \\ \left. + \sum_{n=0}^{\infty} \sum_{k=0}^n \left[-(n+1)r_2^{-(n+2)} \left(\frac{z}{r_1} \frac{\partial r_2}{\partial r_1} - \frac{\sin \theta_1}{r_1} \frac{\partial r_2}{\partial \theta_1} \right) P_n^k(q_2) + r_2^{-(n+1)} \frac{\partial P_n^k(q_2)}{\partial z} \right] f_2 \right\} \quad (5.13)$$

where

$$\frac{\partial r_2}{\partial r_1} = \frac{[r_1 + (b_{12} \sin \theta_1 \cos \varphi_1 + c_{12} \sin \theta_1 \sin \varphi_1 + d_{12} \cos \theta_1)]}{\sqrt{2r_1(b_{12} \sin \theta_1 \cos \varphi_1 + c_{12} \sin \theta_1 \sin \varphi_1 + d_{12} \cos \theta_1) + r_1^2 + b_{12}^2 + c_{12}^2 + d_{12}^2}} \quad (5.14)$$

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and

$$\frac{\partial r_2}{\partial \theta_1} = \frac{r_1 (b_{12} \cos \theta_1 \cos \varphi_1 + c_{12} \cos \theta_1 \sin \varphi_1 - d_{12} \sin \theta_1)}{\sqrt{2r_1 (b_{12} \sin \theta_1 \cos \varphi_1 + c_{12} \sin \theta_1 \sin \varphi_1 + d_{12} \cos \theta_1) + r_1^2 + b_{12}^2 + c_{12}^2 + d_{12}^2}} \quad (5.15)$$

$$f_1 = [R_{1kn} \cos(k\varphi_1) + S_{1kn} \sin(k\varphi_1)] \quad (5.16)$$

$$f_2 = [R_{2kn} \cos(k\varphi_2) + S_{2kn} \sin(k\varphi_2)] \quad (5.17)$$

Hence, the utilization of boundary condition (5.2a) results in

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \kappa [X \exp(-\kappa b) - Y \exp(\kappa b)] \exp[i(\alpha x + \beta y)] d\alpha d\beta = \left\{ \begin{aligned} &\sum_{n=0}^{\infty} \sum_{k=0}^n \left[b(n+1) r_{1b}^{-(n+3)} P_n^k(q_{1b}) + r_{1b}^{-(n+1)} \frac{\partial P_n^k(q_1)}{\partial z_{(b)}} \right] f_1 \\ &+ \sum_{n=0}^{\infty} \sum_{k=0}^n \left[-(n+1) r_{2b}^{-(n+2)} \left(\frac{-b}{r_{1b}} \frac{\partial r_2}{\partial r_{1(b)}} - \frac{\sin \theta_{1b}}{r_{1b}} \frac{\partial r_2}{\partial \theta_{1(b)}} \right) P_n^k(q_{2b}) + r_{2b}^{-(n+1)} \frac{\partial P_n^k(q_2)}{\partial z_{(b)}} \right] f_2 \end{aligned} \right\} \quad (5.18a)$$

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \kappa [X \exp(\kappa c) - Y \exp(-\kappa c)] \exp[i(\alpha x + \beta y)] d\alpha d\beta = \left\{ \begin{aligned} &\sum_{n=0}^{\infty} \sum_{k=0}^n \left[-c(n+1) r_{1c}^{-(n+3)} P_n^k(q_{1c}) + r_{1c}^{-(n+1)} \frac{\partial P_n^k(q_1)}{\partial z_{(c)}} \right] f_1 \\ &+ \sum_{n=0}^{\infty} \sum_{k=0}^n \left[-(n+1) r_{2c}^{-(n+2)} \left(\frac{c}{r_{1c}} \frac{\partial r_2}{\partial r_{1(c)}} - \frac{\sin \theta_{1c}}{r_{1c}} \frac{\partial r_2}{\partial \theta_{1(c)}} \right) P_n^k(q_{2c}) + r_{2c}^{-(n+1)} \frac{\partial P_n^k(q_2)}{\partial z_{(c)}} \right] f_2 \end{aligned} \right\} \quad (5.18b)$$

where $r_{1b}, r_{1c} = r_{1(z=b,c)}$, $r_{2b}, r_{2c} = r_{2(z=b,c)}$, $\theta_{1b}, \theta_{1c} = \theta_{1(z=b,c)}$, $q_{1b}, q_{1c} = q_{1(z=b,c)}$.

Equations (5.18a) and (5.18b) are the two dimensional representations of a Complex Fourier integral,

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} f(\alpha, \beta) \exp[i(\alpha x + \beta y)] d\alpha d\beta = f(x, y) \quad (5.19)$$

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Therefore, $f(\alpha, \beta)$ can be expressed using two dimensional Complex Fourier transforms,

$$f(\alpha, \beta) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} f(x, y) \exp[-i(\alpha x + \beta y)] dx dy \quad (5.20)$$

The above result can be employed to express equations (5.18a) and (5.18b) in the form,

$$f_1(\alpha, \beta) = \kappa [X \exp(-\kappa b) - Y \exp(\kappa b)] = \frac{1}{2\pi} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} f_1(x, y) \exp[-i(\alpha x + \beta y)] dx dy \quad (5.21)$$

$$f_2(\alpha, \beta) = \kappa [X \exp(\kappa c) - Y \exp(-\kappa c)] = \frac{1}{2\pi} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} f_2(x, y) \exp[-i(\alpha x + \beta y)] dx dy \quad (5.22)$$

Equations (5.21) and (5.22) can be solved for X and Y leading to the solutions,

$$X = \frac{1}{2\pi\kappa [\exp(-2\kappa b) - \exp(2\kappa c)]} \left\{ \begin{array}{l} \exp(-\kappa b) \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} A(x, y) \exp[-i(\alpha x + \beta y)] dx dy \\ - \exp(\kappa c) \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} B(x, y) \exp[-i(\alpha x + \beta y)] dx dy \end{array} \right\} \quad (5.23)$$

$$Y = X \exp(-2\kappa b) - \frac{\exp(-\kappa b)}{2\pi\kappa} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} A(x, y) \exp[-i(\alpha x + \beta y)] dx dy \quad (5.24)$$

The functions $A(x, y)$ and $B(x, y)$ in the above equations are expressed as

$$\begin{aligned} A(x, y) = & \sum_{n=0}^{\infty} \sum_{k=0}^n \left[b(n+1) r_{1b}^{-(n+3)} P_n^k(q_{1b}) + r_{1b}^{-(n+1)} \frac{\partial P_n^k(q_1)}{\partial z_{(b)}} \right] f_1 \\ & + \sum_{n=0}^{\infty} \sum_{k=0}^n \left[-(n+1) r_{2b}^{-(n+2)} \left(\frac{-b}{r_{1b}} \frac{\partial r_2}{\partial r_{1(b)}} - \frac{\sin \theta_{1b}}{r_{1b}} \frac{\partial r_2}{\partial \theta_{1(b)}} \right) P_n^k(q_{2b}) + r_{2b}^{-(n+1)} \frac{\partial P_n^k(q_2)}{\partial z_{(b)}} \right] f_2 \end{aligned} \quad (5.25)$$

$$\begin{aligned} B(x, y) = & \sum_{n=0}^{\infty} \sum_{k=0}^n \left[-c(n+1) r_{1c}^{-(n+3)} P_n^k(q_{1c}) + r_{1c}^{-(n+1)} \frac{\partial P_n^k(q_1)}{\partial z_{(c)}} \right] f_1 \\ & + \sum_{n=0}^{\infty} \sum_{k=0}^n \left[-(n+1) r_{2c}^{-(n+2)} \left(\frac{c}{r_{1c}} \frac{\partial r_2}{\partial r_{1(c)}} - \frac{\sin \theta_{1c}}{r_{1c}} \frac{\partial r_2}{\partial \theta_{1(c)}} \right) P_n^k(q_{2c}) + r_{2c}^{-(n+1)} \frac{\partial P_n^k(q_2)}{\partial z_{(c)}} \right] f_2 \end{aligned} \quad (5.26)$$

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Substituting equations (5.25) and (5.26) into equations (5.23) and (5.24) and employing a variable transformation (from x and y to ρ and φ_1), X and Y are re-expressed as

$$X = \frac{1}{2\pi\kappa [\exp(-2\kappa b) - \exp(2\kappa c)]} \left\{ \begin{aligned} &\exp(-\kappa b) \sum_{n=0}^{\infty} \sum_{k=0}^n (I_1 + I_2 + I_3 + I_4) \\ &-\exp(\kappa c) \sum_{n=0}^{\infty} \sum_{k=0}^n (I_5 + I_6 + I_7 + I_8) \end{aligned} \right\} \quad (5.27)$$

$$Y = \frac{1}{2\pi\kappa [\exp(-2\kappa b) - \exp(2\kappa c)]} \left\{ \begin{aligned} &\exp[-\kappa(b-2c)] \sum_{n=0}^{\infty} \sum_{k=0}^n (I_1 + I_2 + I_3 + I_4) \\ &-\exp[-\kappa(2b-c)] \sum_{n=0}^{\infty} \sum_{k=0}^n (I_5 + I_6 + I_7 + I_8) \end{aligned} \right\} \quad (5.28)$$

The definite integrals in equations (5.27) and (5.28) are expressed as

$$I_1 = \left\{ \begin{aligned} &b(n+1) \int_0^{\infty} \int_0^{2\pi} \rho (\rho^2 + b^2)^{-(n+3)/2} P_n^k(q_{1b}) [R_{1kn} \cos(k\varphi_1) + S_{1kn} \sin(k\varphi_1)] \\ &\exp[-i(\rho\alpha \cos \varphi_1 + \rho\beta \sin \varphi_1)] d\rho d\varphi_1 \end{aligned} \right\} \quad (5.29)$$

$$I_2 = \left\{ \begin{aligned} &\int_0^{\infty} \int_0^{2\pi} (\rho^2 + b^2)^{-(n+1)/2} \frac{\partial P_n^k(q_1)}{\partial z_{(b)}} [R_{1kn} \cos(k\varphi_1) + S_{1kn} \sin(k\varphi_1)] \\ &\exp[-i(\rho\alpha \cos \varphi_1 + \rho\beta \sin \varphi_1)] d\rho d\varphi_1 \end{aligned} \right\} \quad (5.30)$$

$$I_3 = \left\{ \begin{aligned} &-(n+1) \int_0^{\infty} \int_0^{2\pi} r_{2b}^{-(n+2)} \left(\frac{-b}{r_{1b}} \frac{\partial r_2}{\partial r_{1(b)}} - \frac{\sin \theta_{1b}}{r_{1b}} \frac{\partial r_2}{\partial \theta_{1(b)}} \right) P_n^k(q_{2b}) \\ &[R_{2kn} \cos(k\varphi_2) + S_{2kn} \sin(k\varphi_2)] \exp[-i(\rho\alpha \cos \varphi_1 + \rho\beta \sin \varphi_1)] d\rho d\varphi_1 \end{aligned} \right\} \quad (5.31)$$

$$I_4 = \left\{ \begin{aligned} &\int_0^{\infty} \int_0^{2\pi} r_{2b}^{-(n+1)} \frac{\partial P_n^k(q_2)}{\partial z_{(b)}} [R_{2kn} \cos(k\varphi_2) + S_{2kn} \sin(k\varphi_2)] \\ &\exp[-i(\rho\alpha \cos \varphi_1 + \rho\beta \sin \varphi_1)] d\rho d\varphi_1 \end{aligned} \right\} \quad (5.32)$$

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$$I_5 = \left\{ \int_0^\infty \int_0^{2\pi} \rho (\rho^2 + c^2)^{-(n+3)/2} P_n^k(q_{1c}) [R_{1kn} \cos(k\varphi_1) + S_{1kn} \sin(k\varphi_1)] \exp[-i(\rho\alpha \cos \varphi_1 + \rho\beta \sin \varphi_1)] d\rho d\varphi_1 \right\} \quad (5.33)$$

$$I_6 = \left\{ \int_0^\infty \int_0^{2\pi} (\rho^2 + c^2)^{-(n+1)/2} \frac{\partial P_n^k(q_1)}{\partial z_{(c)}} [R_{1kn} \cos(k\varphi_1) + S_{1kn} \sin(k\varphi_1)] \exp[-i(\rho\alpha \cos \varphi_1 + \rho\beta \sin \varphi_1)] d\rho d\varphi_1 \right\} \quad (5.34)$$

$$I_7 = \left\{ -(n+1) \int_0^\infty \int_0^{2\pi} r_{2c}^{-(n+2)} \left(\frac{c}{r_{1c}} \frac{\partial r_2}{\partial r_{1(c)}} - \frac{\sin \theta_{1c}}{r_{1c}} \frac{\partial r_2}{\partial \theta_{1(c)}} \right) P_n^k(q_{2c}) [R_{2kn} \cos(k\varphi_2) + S_{2kn} \sin(k\varphi_2)] \exp[-i(\rho\alpha \cos \varphi_1 + \rho\beta \sin \varphi_1)] d\rho d\varphi_1 \right\} \quad (5.35)$$

$$I_8 = \left\{ \int_0^\infty \int_0^{2\pi} r_{2c}^{-(n+1)} \frac{\partial P_n^k(q_2)}{\partial z_{(c)}} [R_{2kn} \cos(k\varphi_2) + S_{2kn} \sin(k\varphi_2)] \exp[-i(\rho\alpha \cos \varphi_1 + \rho\beta \sin \varphi_1)] d\rho d\varphi_1 \right\} \quad (5.36)$$

5.3.2.1 Hankel transformation for k -fold symmetric functions

It can be observed that the integrands appearing inside the integrals I_1 , I_2 , I_5 , I_6 have k -fold symmetry. This means that the integrands $f(x, y)$ can be expressed in the form, $f(\rho, \varphi_1) \exp(ik\varphi_1)$. Hence, the φ_1 integration can be performed analytically using k^{th} order Hankel transforms. To help follow the mathematical development here, the transformation of integral I_1 is described here.

Employing two complex transformations, $x + iy = \rho \exp(i\varphi_1)$, and $\alpha + i\beta = \kappa \exp(i\xi)$, integral I_1 can be expressed as

$$I_1 = \left\{ b(n+1) \int_0^\infty \int_0^{2\pi} \rho f(\rho) [R_{1kn} \cos(k\varphi_1) + S_{1kn} \sin(k\varphi_1)] \exp[-i\kappa\rho \cos(\varphi_1 - \xi)] d\rho d\varphi_1 \right\} \quad (5.37)$$

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$$\text{where } f(\rho) = (\rho^2 + b^2)^{-(n+3)/2} P_n^k(q_{1b}). \quad (5.38)$$

Now let $I_1 = I_{1C} + I_{1S}$

where

$$I_{1C} = b(n+1) \int_0^\infty \int_0^{2\pi} \rho f(\rho) R_{1kn} \cos(k\varphi_1) \exp[-i\kappa\rho \cos(\varphi_1 - \xi)] d\rho d\varphi_1 \quad (5.39)$$

$$I_{1S} = b(n+1) \int_0^\infty \int_0^{2\pi} \rho f(\rho) S_{1kn} \sin(k\varphi_1) \exp[-i\kappa\rho \cos(\varphi_1 - \xi)] d\rho d\varphi_1 \quad (5.40)$$

Now, using the relation,

$$\int_0^{2\pi} \exp(\cos(x-a)) \cos kx dx = \int_0^{2\pi} \exp(\cos(x)) \cos k(x-a) dx,$$

$$I_{1C} = b(n+1) \left\{ \begin{aligned} &\cos k\xi \int_0^\infty \rho f(\rho) \int_0^{2\pi} \exp[-i\kappa\rho \cos \varphi_1] \cos k\varphi_1 d\varphi_1 d\rho \\ &+ \sin k\xi \int_0^\infty \rho f(\rho) \int_0^{2\pi} \exp[-i\kappa\rho \cos \varphi_1] \sin k\varphi_1 d\varphi_1 d\rho \end{aligned} \right\} \quad (5.41)$$

The complex exponential expressions for the trigonometric functions can be given as

$$\cos(k\varphi_1) = \left(\frac{\exp(ik\varphi_1) + \exp(-ik\varphi_1)}{2} \right) \quad (5.42)$$

$$\sin(k\varphi_1) = \left(\frac{\exp(ik\varphi_1) - \exp(-ik\varphi_1)}{2i} \right) \quad (5.43)$$

Also, the Bessel functions of the first kind $J_k(z)$ have the integral representations,

$$J_n(z) = \frac{1}{2\pi(i)^n} \int_0^{2\pi} \exp(iz \cos \varphi) \exp(in\varphi) d\varphi \quad (5.44)$$

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Substituting equation (5.42), (5.43) in (5.41) and employing equation (5.44), results in the following equation after rearrangement,

$$\begin{aligned} I_{1c} &= \frac{\cos k\xi}{i^k} \int_0^\infty \rho f(\rho) \left[(-1)^k \pi J_k(-\kappa\rho) + \pi(-1)^k J_k(-\kappa\rho) \right] d\rho \\ &= i^k 2\pi \cos k\xi \int_0^\infty \rho f(\rho) J_k(-\kappa\rho) d\rho \end{aligned} \quad (5.45)$$

Similarly, I_{1s} can be expressed as

$$I_{1s} = (i)^k 2\pi \sin k\xi \int_0^\infty \rho F(\rho) J_k(-\kappa\rho) d\rho \quad (5.46)$$

Using the above procedure, integrals I_1 , I_2 , I_5 and I_6 are transformed to single integrals,

$$I_1 = (i)^k 2\pi b(n+1) \int_0^\infty \left\{ \rho (\rho^2 + b^2)^{-(n+3)/2} P_n^k(q_{1b}) J_k(-\kappa\rho) \right\} d\rho \quad (5.47)$$

$$I_2 = (i)^k 2\pi \int_0^\infty \left\{ \rho (\rho^2 + b^2)^{-(n+1)/2} \frac{\partial P_n^k(q_1)}{\partial z_{(b)}} J_k(-\kappa\rho) \right\} d\rho \quad (5.48)$$

$$I_5 = -(i)^k 2\pi c(n+1) \int_0^\infty \left\{ \rho (\rho^2 + c^2)^{-(n+3)/2} P_n^k(q_{1c}) J_k(-\kappa\rho) \right\} d\rho \quad (5.49)$$

$$I_6 = -(i)^k 2\pi c(n+1) \int_0^\infty \left\{ \rho (\rho^2 + c^2)^{-(n+3)/2} \frac{\partial P_n^k(q_1)}{\partial z_{(c)}} J_k(-\kappa\rho) \right\} d\rho \quad (5.50)$$

5.3.2.2 Generalized Hankel transformation

The integrands $f(\rho, \varphi_1)$ in the integrals I_3 , I_4 , I_7 and I_8 do not possess any symmetry and are arbitrary functions of ρ and φ_1 . Hence, these integrals are transformed using the

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generalized Hankel transforms. These transforms for an arbitrary function $f(\rho, \varphi)$ is defined as follows (Athale et al., 1982):

$$f(\rho, \varphi_1) = \sum_{n=-\infty}^{\infty} f_n(\rho) \exp(ik\varphi_1) \quad (5.51)$$

$$H_{nn}(\kappa) = \int_0^{\infty} f_n(\rho) J_n(\kappa\rho) \rho d\rho \quad (5.52)$$

The generalized Hankel transform $H_{nn}(\kappa)$ thus involves a Fourier series expansion of $f(\rho, \varphi_1)$ with respect to φ_1 followed by the operation of the Hankel transform of order n on $f_n(\rho)$.

The integrals I_3 , I_4 , I_7 and I_8 after substituting for r_2 , θ_2 and φ_2 in terms of r_1 , θ_1 and φ_1 can be expressed as

$$I_3 = \int_0^{\infty} \int_0^{2\pi} f_1(\rho, \varphi_1) f_2(\rho, \varphi_1) f_3(\rho, \varphi_1) d\rho d\varphi_1 \quad (5.53)$$

$$f_1(\rho, \varphi_1) = \rho \left[\frac{2\sqrt{\rho^2 + b^2} (b_{12} \sin \theta_{1b} \cos \varphi_1 + c_{12} \sin \theta_{1b} \sin \varphi_1 + d_{12} \cos \theta_{1b})}{+\sqrt{\rho^2 + b^2} + b_{12}^2 + c_{12}^2 + d_{12}^2} \right]^{-(n+3)/2} \quad (5.54)$$

$$f_2(\rho, \varphi_1) = P_n^k(q_{2b}) \left[\begin{array}{l} b + \frac{b_{12} \sin \theta_{1b} \cos \varphi_1}{\sqrt{\rho^2 + b^2}} b + \frac{c_{12} \sin \theta_{1b} \sin \varphi_1}{\sqrt{\rho^2 + b^2}} b + \frac{d_{12} \cos \theta_{1b}}{\sqrt{\rho^2 + b^2}} b - \\ b_{12} \cos \varphi_1 \sin \theta_{1b} \cos \theta_{1b} - c_{12} \sin \varphi_1 \sin \theta_{1b} \cos \theta_{1b} - d_{12} \sin^2 \theta_{1b} \end{array} \right] \quad (5.55)$$

$$f_3(\rho, \varphi_1) = \left\{ \begin{array}{l} R_{2kn} \cos \left[k \tan^{-1} \left(\frac{\sqrt{\rho^2 + b^2} \sin \theta_1 \sin \varphi_1 + c_{12}}{\sqrt{\rho^2 + b^2} \sin \theta_1 \cos \varphi_1 + b_{12}} \right) \right] + \\ S_{2kn} \sin \left[k \tan^{-1} \left(\frac{\sqrt{\rho^2 + b^2} \sin \theta_1 \sin \varphi_1 + c_{12}}{\sqrt{\rho^2 + b^2} \sin \theta_1 \cos \varphi_1 + b_{12}} \right) \right] \\ \exp[-i(\rho\alpha \cos \varphi_1 + \rho\beta \sin \varphi_1)] \end{array} \right\} \quad (5.56)$$

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$$I_4 = \int_0^\infty \int_0^{2\pi} f_4(\rho, \varphi_1) f_3(\rho, \varphi_1) d\rho d\varphi_1 \quad (5.57)$$

$$f_4(\rho, \varphi_1) = \frac{\partial P_n^k(q_2)}{\partial z_{(b)}} \rho \left[\frac{2\sqrt{\rho^2 + b^2} \left(b_{12} \sin \theta_{1b} \cos \varphi_1 + c_{12} \sin \theta_{1b} \sin \varphi_1 \right) + d_{12} \cos \theta_{1b}}{+\sqrt{\rho^2 + b^2} + b_{12}^2 + c_{12}^2 + d_{12}^2} \right]^{-(n+1)/2} \quad (5.58)$$

$$I_7 = \int_0^\infty \int_0^{2\pi} f_5(\rho, \varphi_1) f_6(\rho, \varphi_1) f_7(\rho, \varphi_1) d\rho d\varphi_1 \quad (5.59)$$

$$f_5(\rho, \varphi_1) = \rho \left[\frac{2\sqrt{\rho^2 + c^2} \left(b_{12} \sin \theta_{1c} \cos \varphi_1 + c_{12} \sin \theta_{1c} \sin \varphi_1 + d_{12} \cos \theta_{1b} \right)}{+\sqrt{\rho^2 + c^2} + b_{12}^2 + c_{12}^2 + d_{12}^2} \right]^{-(n+3)/2} \quad (5.60)$$

$$f_6(\rho, \varphi_1) = P_n^k(q_{2c}) \left[\begin{aligned} &c + \frac{b_{12} \sin \theta_{1b} \cos \varphi_1}{\sqrt{\rho^2 + c^2}} c + \frac{c_{12} \sin \theta_{1b} \sin \varphi_1}{\sqrt{\rho^2 + c^2}} c + \frac{d_{12} \cos \theta_{1c}}{\sqrt{\rho^2 + c^2}} c \\ &- b_{12} \cos \varphi_1 \sin \theta_{1b} \cos \theta_{1b} - c_{12} \sin \varphi_1 \sin \theta_{1b} \cos \theta_{1b} - d_{12} \sin^2 \theta_{1b} \end{aligned} \right] \quad (5.61)$$

$$f_7(\rho, \varphi_1) = \left\{ \begin{aligned} &\left[R_{2kn} \cos \left[k \tan^{-1} \left(\frac{\sqrt{\rho^2 + c^2} \sin \theta_1 \sin \varphi_1 + c_{12}}{\sqrt{\rho^2 + c^2} \sin \theta_1 \cos \varphi_1 + b_{12}} \right) \right] + \right. \\ &\left. S_{2kn} \sin \left[k \tan^{-1} \left(\frac{\sqrt{\rho^2 + c^2} \sin \theta_1 \sin \varphi_1 + c_{12}}{\sqrt{\rho^2 + c^2} \sin \theta_1 \cos \varphi_1 + b_{12}} \right) \right] \right] \\ &\exp[-i(\rho\alpha \cos \varphi_1 + \rho\beta \sin \varphi_1)] \end{aligned} \right\} \quad (5.62)$$

$$I_8 = \int_0^\infty \int_0^{2\pi} f_8(\rho, \varphi_1) f_7(\rho, \varphi_1) d\rho d\varphi_1 \quad (5.63)$$

$$f_8(\rho, \varphi_1) = \frac{\partial P_n^k(q_2)}{\partial z_{(c)}} \rho \left[\frac{2\sqrt{\rho^2 + c^2} \left(b_{12} \sin \theta_{1b} \cos \varphi_1 + c_{12} \sin \theta_{1b} \sin \varphi_1 \right) + d_{12} \cos \theta_{1b}}{+\sqrt{\rho^2 + c^2} + b_{12}^2 + c_{12}^2 + d_{12}^2} \right]^{-(n+1)/2} \quad (5.64)$$

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5.3.2.3 Polynomial expansion of Legendre functions for outer (ρ) integration

In order to perform the outer integration with respect to variable ρ , the finite series expressions of Associated Legendre functions and the integral representations of the modified Bessel functions of the second kind are employed.

The finite series representation of associated Legendre polynomial $P_n^k(q)$ can be given as (Erdelyi et al., 1954),

$$P_n^k(q_1) = (-1)^k \frac{(1-q^2)^{k/2}}{2^n} \sum_{s=0}^{[n/2]} \frac{(-1)^s (2n-2s)!}{s!(n-s)!(n-2s)!} \frac{\Gamma(n-2s+1)}{\Gamma(n-2s-k+1)} q_1^{n-2s-k} \quad (5.65)$$

where $\Gamma(x)$ represents the Gamma function and $[x]$ represents the largest integer less than or equal to x . It should be noted that, $P_n^k(q) = 0$ for $k > n$.

The derivative of the Legendre polynomial with respect to z has the expression,

$$\frac{\partial P_n^k(q_1)}{\partial z} = \frac{\partial P_n^k(q_1)}{\partial q_1} \frac{\partial q_1}{\partial z} \quad (5.66)$$

The derivative of the Legendre polynomial with respect to its argument can in turn be represented using recurrence relations,

$$\frac{dP_n^k(q_1)}{dq_1} = \frac{(n+1)q_1 P_n^k(q_1) - (n-k+1)P_{(n+1)}^k(q_1)}{1-q_1^2} \quad (5.67)$$

Noting that $\frac{\partial q_1}{\partial z} = \frac{\rho^2}{r_1^3}$ equation (5.66) is written as

$$\frac{\partial P_n^k(q_1)}{\partial z} = \frac{\rho^2}{r_1^3} \left(\frac{(n+1)q_1 P_n^k(q_1) - (n-k+1)P_{(n+1)}^k(q_1)}{1-q_1^2} \right) \quad (5.68)$$

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Similarly,

$$\frac{\partial P_n^k(q_2)}{\partial z} = \frac{\partial q_2}{\partial z} \left(\frac{(n+1)q_2 P_n^k(q_2) - (n-k+1)P_{(n+1)}^k(q_2)}{1-q_2^2} \right) \quad (5.69)$$

where

$$\frac{\partial q_2}{\partial z} = \frac{\partial}{\partial z} \left\{ \cos \left\{ \tan^{-1} \left[\frac{r_1^2 \sin \theta_1 + b_{12}^2 + c_{12}^2 + 2r_1 \sin \theta_1 (b_{12} \cos \varphi_1 + c_{12} \sin \varphi_1)^{1/2}}{d_{12} + r_1 \cos \theta_1} \right] \right\} \right\} \quad (5.70)$$

$$\frac{\partial q_2}{\partial z} = f(r_1, \theta_1, \theta_2) \left\{ \begin{array}{l} \frac{d_{12} + r_1 \cos \theta_1}{2\sqrt{r_1^2 \sin \theta_1 + b_{12}^2 + c_{12}^2 + 2r_1 \sin \theta_1 (b_{12} \cos \varphi_1 + c_{12} \sin \varphi_1)}} \\ \left[\frac{2z \sin \theta_1 - 2\rho \cos \theta_1}{r_1} (b_{12} \cos \varphi_1 + c_{12} \sin \varphi_1) \right] \\ -\rho \cos \theta_1 + 2z \sin \theta_1 \\ -\sqrt{r_1^2 \sin \theta_1 + b_{12}^2 + c_{12}^2 + 2r_1 \sin \theta_1 (b_{12} \cos \varphi_1 + c_{12} \sin \varphi_1)}} \\ \left(\frac{z \cos \theta_1 - \rho \cos \theta_1}{r_1} \right) \end{array} \right\} \quad (5.71)$$

$$\text{where } f(r_1, \theta_1, \theta_2) = \frac{-\sin \theta_2}{(1 + \tan^2 \theta_2)(d_{12} + r_1 \cos \theta_1)^2} \quad (5.72)$$

Substituting equation (5.65) in equation (5.68) we get

$$\frac{\partial P_n^k(q_1)}{\partial z} \underset{(b)}{=} \frac{(-1)^k \rho^k}{2^n (\rho^2 + b^2)^{(k+1)/2}} \left[\frac{b(n+1)}{\sqrt{\rho^2 + b^2}} \sum_{s=0}^{[n/2]} \frac{(-1)^s (2n-2s)! f_{1nsk} q^{n-2s-k}}{s!(n-s)!(n-2s)!} \right. \\ \left. - (n-k+1) \sum_{s=0}^{[(n+1)/2]} \frac{(-1)^s [2(n+1)-2s]! f_{2nsk} q^{n+1-2s-k}}{s!(n+1-s)!(n+1-2s)!} \right] \quad (5.73)$$

$$f_{1nsk} = \frac{\Gamma(n-2s+1)}{\Gamma(n-2s-k+1)}, \quad f_{2nsk} = \frac{\Gamma(n-2s+2)}{\Gamma(n-2s-k+2)} \quad (5.74)$$

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Equation (5.73), after algebraic manipulation, becomes

$$\frac{\partial P_n^k(q_1)}{\partial z} \Big|_{(b)} = \left[\begin{aligned} & \frac{\rho^k b(n+1)}{2^n} \sum_{s=0}^{[n/2]} \frac{(-1)^{s+k} (2n-2s)! f_{1nsk}(-b)^{n-2s-k}}{s!(n-s)!(n-2s)! (\rho^2 + b^2)^{(n-2s+1)/2}} \\ & - \frac{(n-k+1)\rho^k}{2^n} \sum_{s=0}^{[(n+1)/2]} \frac{(-1)^{s+k} [2(n+1)-2s]! f_{2nsk}(-b)^{n+1-2s-k}}{s!(n+1-s)!(n+1-2s)! (\rho^2 + b^2)^{(n-2s+1)/2}} \end{aligned} \right] \quad (5.75)$$

Similarly, $\frac{\partial P_n^k(q_1)}{\partial z} \Big|_{(c)}$ can be represented by replacing $-b$ in equation (5.75) by c . The

above expressions for Legendre polynomials and its derivatives can be substituted into the integrals I_1 , I_2 , I_5 and I_6 that are now represented by single integrals of the variable, ρ .

A careful observation on the expressions for $P_n^k(q)$ and $\frac{\partial P_n^k(q)}{\partial z}$ would reveal that the term ρ^k in the equation factor out. Also, the expressions for the integrals I_1 , I_2 , I_5 and I_6 appear in as $\rho J_k(-\kappa\rho)(\rho^2 + z^2)^m$ where z can be $-b$ or c , and m is arbitrary. Hence, to evaluate these integrals analytically, an integral representation of the modified Bessel functions of the second kind is employed (Abramowitz and Stegun, 1985).

$$\int_0^\infty \frac{x^{n+1} J_n(bx)}{(x^2 + a^2)^{m+1}} dx = \frac{a^{n-m} b^m}{2^m \Gamma(m+1)} K_{n-m}(ab) \quad (5.76)$$

Hence,

$$\int_0^\infty \frac{\rho^{k+1} J_k(-\kappa\rho)}{(\rho^2 + z^2)^{m+1}} d\rho = \frac{z^{n-m} (-\kappa)^m}{2^m \Gamma(m+1)} K_{k-m}(\kappa|z|) \quad (5.77)$$

In the above equations $K_n(x)$ represents the modified Bessel function of the second kind.

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Hence, the integrals I_1, I_2, I_5, I_6 can be expressed as

$$I_1(\kappa) = \sum_{s=0}^{[n/2]} \frac{(-1)^{s+1} (2n-2s)!}{s!(n-s)!(n-2s)!} f_{nsk1} \left[\frac{b^{-(s+1/2)} \kappa^{n-s+1/2}}{2^{2n-s+1/2} \Gamma(n-s+3/2)} \right] K_{k-(n-s+1/2)}(\kappa b) \quad (5.78)$$

$$I_2(\kappa) = \left\{ \begin{aligned} & b(n+1) \sum_{s=0}^{[n/2]} \frac{(-1)^{s+1} (2n-2s)!}{s!(n-s)!(n-2s)!} \left[\frac{f_{nsk1} b^{-s} \kappa^{n-s}}{2^{2n-s} \Gamma(n-s+1)} \right] \\ & - (n-k+1) \sum_{s=0}^{[(n+1)/2]} \frac{(-1)^{s+1} [2(n+1)-2s]!}{s!(n+1-s)!(n+1-2s)!} \left[\frac{f_{nsk2} b^{1-s} \kappa^{n-s}}{2^{2n-s} \Gamma(n-s+1)} \right] \end{aligned} \right\} K_{k-n+s}(\kappa b) \quad (5.79)$$

$$I_5(\kappa) = \sum_{s=0}^{[n/2]} \frac{(-1)^{s+1} (2n-2s)!}{s!(n-s)!(n-2s)!} f_{nsk1} \left[\frac{c^{-(s+1/2)} \kappa^{n-s+1/2}}{2^{2n-s+1/2} \Gamma(n-s+3/2)} \right] K_{k-(n-s+1/2)}(\kappa c) \quad (5.80)$$

$$I_6(\kappa) = \left\{ \begin{aligned} & c(n+1) \sum_{s=0}^{[n/2]} \frac{(-1)^{s+1} (2n-2s)!}{s!(n-s)!(n-2s)!} \left[\frac{f_{nsk1} c^{-s} \kappa^{n-s}}{2^{2n-s} \Gamma(n-s+1)} \right] \\ & - (n-k+1) \sum_{s=0}^{[(n+1)/2]} \frac{(-1)^{s+1} [2(n+1)-2s]!}{s!(n+1-s)!(n+1-2s)!} \left[\frac{f_{nsk2} c^{1-s} \kappa^{n-s}}{2^{2n-s} \Gamma(n-s+1)} \right] \end{aligned} \right\} K_{k-n+s}(\kappa c) \quad (5.81)$$

However, the integrals I_3, I_4, I_7, I_8 can not be performed using the above procedure and should be evaluated numerically. These expressions should be substituted into equations (5.27) and (5.28) for X and Y to express the electrical potential distribution as

$$\phi = E_\infty \left[\begin{aligned} & \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} f^*(\kappa) \exp[i(\alpha x + \beta y)] d\alpha d\beta - x \\ & + \sum_{j=1}^2 \sum_{n=0}^{\infty} \sum_{k=0}^n r_j^{-(n+1)} P_n^k(q_j) [R_{jkn} \cos(k\varphi_j) + S_{jkn} \sin(k\varphi_j)] \end{aligned} \right] \quad (5.82)$$

The complicated expression for $f^*(\kappa)$ is provided in Appendix 2. Employing the Hankel transform technique described before (please refer to section 5.3.2), the infinite range double integral in α and β could be converted into single integral in κ ranging from 0 to ∞ . This outer integral cannot be simplified and must be evaluated numerically.

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Now, the boundary condition on the sphere surfaces (equation (5.2b)) can be applied to yield

$$\frac{\partial \phi}{\partial r_{1(a_1)}} = (\phi'_{w1c} + \phi'_{w2nc} + \phi'_s)_{(a_1)} = 0 \quad (5.83)$$

$$\frac{\partial \phi}{\partial r_{2(a_2)}} = (\phi'_{w1nc} + \phi'_{w2nc} + \phi'_s)_{(a_2)} = 0 \quad (5.84)$$

In the above equations, subscript “c” stands for circular symmetry and subscript “nc” stands for non-symmetry. The expressions for ϕ'_{w1c} , ϕ'_{w2c} , ϕ'_{w1nc} , ϕ'_{w2nc} and ϕ'_s being lengthy and complicated, are provided in Appendix 2.

5.3.3 Boundary Collocation and Electrical potential distribution

To satisfy the boundary condition on the entire surface of the sphere would require the solution of the entire infinite array of unknown constants R_{jkn} . However, the boundary collocation technique (Ganatos et al., 1990) is based on the truncation of this infinite series, and for the case of two spheres moving in the same plane (x - z plane, in the present study), the boundary conditions can be enforced on a finite number of points on the generating circular arc (from $\theta_1, \theta_2 = 0$ to π). If the infinite series in equation is truncated after $k = K$ and $n = N$ terms, equations (5.83) and (5.84) represent $2KN$ linear algebraic equations with equal number of unknowns that can be solved by standard matrix inversion technique. The accuracy of the boundary collocation/truncation technique can be improved to any degree by taking sufficient large value of K and M . In the present study, $K = 100$ and $M = 100$ was used to achieve results with an error less than 10^{-5} . Naturally, as $M \rightarrow \infty$, the truncation error vanishes and the overall accuracy of the

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solution depends only upon the numerical integration required in evaluating the matrix elements. The numerical integrations in the present study were performed using 180 point Gauss-Laugerre quadrature. However, it has to be noted that the matrix equations corresponding to equations (5.83) and (5.84) become singular if $\theta_1, \theta_2 = 0, \pi/2, \pi$. To surpass this difficulty, these points are replaced by closely adjacent points $\theta_1/\theta_2 = \delta, \pi/2 - \delta, \pi/2 + \delta$ and $\pi - \delta$ (Keh et al., 2002a). The optimum value of δ in this study is found to be 0.15° .

5.4 Fluid velocity distribution

Knowing the electrical potential distribution in the fluid, the fluid velocity distribution can now be computed. The fluid velocity at an arbitrary point P in space due to the two spheres can be expressed as the superposition of Lamb's fundamental solution for a single sphere (Hassonjee et al., 1988).

5.4.1 Governing equations and boundary conditions

The governing equations of motion for the fluid are represented as

$$\mu \nabla^2 \mathbf{V} - \nabla p = 0, \quad \nabla \cdot \mathbf{V} = 0 \quad (5.85)$$

Because the applied electric field interacts with the double layer at the nonconducting solid surface (of both the sphere and the wall) to produce a relative tangential fluid velocity at the surface of the double layer, the boundary conditions on the particle surfaces and the channel wall are expressed as (Keh and Anderson, 1985)

$$\mathbf{V}_w = \frac{\epsilon_0 \epsilon_r \zeta_w}{\eta} \nabla \phi \quad \text{at } z = -b, z = c \quad (5.86)$$

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$$\mathbf{V} = \mathbf{U}_1 + \mathbf{r}_1 \times \boldsymbol{\omega}_1 + \frac{\varepsilon_0 \varepsilon_r \zeta_{p1}}{\eta} \nabla \phi \text{ at } r_1 = a_1 \text{ (surface of particle 1)} \quad (5.87)$$

$$\mathbf{V} = \mathbf{U}_2 + \mathbf{r}_2 \times \boldsymbol{\omega}_2 + \frac{\varepsilon_0 \varepsilon_r \zeta_{p2}}{\eta} \nabla \phi \text{ at } r_2 = a_2 \text{ (surface of particle 2)} \quad (5.88)$$

$$\text{where } \nabla \phi = \frac{\partial \phi}{\partial r} \hat{\mathbf{e}}_r + \frac{1}{r} \frac{\partial \phi}{\partial \theta} \hat{\mathbf{e}}_\theta + \frac{1}{r \sin \theta} \frac{\partial \phi}{\partial \varphi} \hat{\mathbf{e}}_\varphi \quad (5.89)$$

where $\mathbf{U}_1$, $\boldsymbol{\omega}_1$ and $\mathbf{U}_2$, $\boldsymbol{\omega}_2$ represent the translational and rotational velocities of spheres 1 and 2, respectively. ζ_{p1} and ζ_{p2} represent the zeta potentials of particles 1 and 2, respectively. Equation (5.88) and (5.89) gives the coupling between the electric field and the fluid motion, and the potential distribution $\phi(x, y, z)$ is determined from equation (5.8).

In view of the linearity of the governing equations, the velocity field $\mathbf{V}$ can be decomposed into three parts (Ganatos et al., 1980):

$$\mathbf{V} = \mathbf{V}_\infty + \mathbf{V}_s + \mathbf{V}_w \quad (5.90)$$

where $\mathbf{V}_w$ and $\mathbf{V}_s$ represents the disturbance to the flow field caused due to the presence of the plane walls and the spheres, respectively. $\mathbf{V}_\infty$ represents the flow profile between the parallel plates far removed from the spheres. $\mathbf{V}_\infty$ is expressed as

$$\mathbf{V}_\infty = -\frac{\varepsilon_0 \varepsilon_r \zeta_w}{\eta} E_\infty \mathbf{i} \quad (5.91)$$

The above equation represents the uniform electroosmotic flow velocity of the fluid between the parallel plates.

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The velocity disturbance caused by the two plane walls can be expressed by a general Fourier integral solution to the Stokes equation in Cartesian coordinates, originally derived by Faxen (1923). The basis of Faxen's method is to express the fundamental solution of Laplace equation

$$\nabla^2 p = 0 \quad (5.92)$$

which is $p = -\frac{1}{4\pi r}$ in integral form. This is done by expressing $\frac{1}{r}$ in the following form:

$$\frac{1}{r} = \frac{1}{2\pi} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \exp[i(\alpha x + \beta y) - \kappa |z|] \frac{d\alpha d\beta}{\kappa} \quad (5.93)$$

This function and its partial derivatives may be employed to express Stoke's original solution for a sphere in an infinite medium entirely in terms of a Cartesian coordinate system. The general solution to equation (5.85) can then be given as

$$\mathbf{V}_w = V_{wx} \mathbf{i} + V_{wy} \mathbf{j} + V_{wz} \mathbf{k} \quad (5.94)$$

where

$$V_{wx} = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \left\{ \begin{aligned} &\exp(-\kappa z) \left[\frac{i\alpha}{\kappa} G_1 + \frac{2}{\kappa} G_2 - \frac{\alpha^2}{\kappa^3} (1 + \kappa z) G_2 + \frac{z\alpha^2}{\kappa} G_3 \right] \\ &+ \exp(\kappa z) \left[\frac{i\alpha}{\kappa} G_1' + \frac{2}{\kappa} G_2' - (1 - \kappa z) \frac{\alpha^2}{\kappa^3} G_2' + \frac{z\alpha^2}{\kappa} G_3' \right] \end{aligned} \right\} d\alpha d\beta \quad (5.95)$$

$$V_{wy} = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \left\{ \begin{aligned} &\exp(-\kappa z) \left[\frac{G_1}{\kappa} + \frac{i\alpha}{\kappa^3} G_2 (1 + \kappa z) - \frac{i\alpha z}{\kappa} G_3 \right] \\ &+ \exp(\kappa z) \left[\frac{G_1'}{\kappa} + \frac{i\alpha}{\kappa^3} G_2' (1 - \kappa z) - \frac{i\alpha z}{\kappa} G_3' \right] \end{aligned} \right\} d\alpha d\beta \quad (5.96)$$

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$$V_{wz} = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \left\{ \begin{aligned} &\exp(-\kappa z) \left[-G_1 - \frac{i\alpha z}{\kappa} G_2 + \frac{i\alpha}{\kappa} (1 + \kappa z) G_3 \right] \\ &+ \exp(\kappa z) \left[G_1' - \frac{zi\alpha}{\kappa} G_2' + \frac{i\alpha}{\kappa} (1 - \kappa z) G_3' \right] \\ &\exp[i(\alpha x + \beta y)] \end{aligned} \right\} d\alpha d\beta \quad (5.97)$$

In the above equation, α and β are the separation variables and $\kappa = \sqrt{\alpha^2 + \beta^2}$. The functions G_1 , G_2 , G_3 , G_1' , G_2' and G_3' are functions of α and β .

The fundamental solution of creeping flow equation (equation (5.85)) that is capable of describing an arbitrary disturbance on the surface of a sphere of radius a can be expressed as (Lamb et al., 1945)

$$V_s = \sum_{n=1}^{\infty} \left[\nabla \times (\mathbf{r} \chi_{-(n+1)}) + \nabla \Phi_{-(n+1)} - \frac{(n-2)}{\mu(2n-1)2n} r^2 \nabla P_{-(n+1)} + \frac{(n+1)}{\mu n(2n+1)} \mathbf{r} P_{-(n+1)} \right] \quad (5.98)$$

where $\chi_{-(n+1)}$, $\Phi_{-(n+1)}$ and $P_{-(n+1)}$ represent the solid spherical harmonic functions of order $-(n+1)$ and $\mathbf{r}$ is the radial position vector whose origin lies at the center of the sphere. For N spheres moving slowly in an unbounded, incompressible, Newtonian, quiescent fluid, the linear superposition of N individual spherical solutions yields

$$V_s = \sum_{j=1}^N \sum_{n=1}^{\infty} \left[\nabla \times (\mathbf{r}_j \chi_{-(n+1),j}) + \nabla \Phi_{-(n+1),j} - \frac{(n-2)}{\mu(2n-1)2n} r_j^2 \nabla P_{-(n+1),j} + \frac{(n+1)}{\mu n(2n+1)} \mathbf{r}_j P_{-(n+1),j} \right] \quad (5.99)$$

where $\chi_{-(n+1),j}$, $\Phi_{-(n+1),j}$ and $P_{-(n+1),j}$ are solid spherical harmonic functions of order $(n+1)$ that depend on $\mathbf{r}_j$, θ_j and ϕ_j , the stationary spherical coordinates measured from the centre of the j^{th} sphere at the instant of time under consideration.

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In general, the solid spherical harmonic functions have the following form,

$$\begin{bmatrix} \chi_{-(n+1),j} \\ \Phi_{-(n+1),j} \\ P_{-(n+1),j} \end{bmatrix} = \sum_{k=0}^{\infty} P_n^k(q_j) \frac{1}{r_j^{n+1}} \left\{ \begin{bmatrix} A_{jmn} \\ C_{jmn} \\ E_{jmn} \end{bmatrix} \sin k\varphi_j + \begin{bmatrix} B_{jmn} \\ D_{jmn} \\ F_{jmn} \end{bmatrix} \cos k\varphi_j \right\} \quad (5.100)$$

where $A_{jmn} - F_{jmn}$ are harmonic functions that can be determined by satisfying the boundary conditions on the surface of each particle. Substituting equation (5.100) into equation (5.99), an expression for the fluid velocity field is obtained:

$$\mathbf{V}_s = \sum_{j=1}^2 \sum_{n=1}^{\infty} \sum_{k=0}^n \left[V_{rj}(r_j, \theta_j, \varphi_j) \hat{\mathbf{e}}_{rj} + V_{\theta j}(r_j, \theta_j, \varphi_j) \hat{\mathbf{e}}_{\theta j} + V_{\varphi j}(r_j, \theta_j, \varphi_j) \hat{\mathbf{e}}_{\varphi j} \right] \quad (5.101)$$

where the velocity components are expressed by

$$V_{rj} = \left\{ \begin{aligned} & \frac{-(n+1)}{r_j^{(n+2)}} P_n^k(q_j) (C_{jkn} \cos k\varphi_j + D_{jkn} \sin k\varphi_j) \\ & + \frac{(n+1)}{2\mu(2n-1)} \frac{P_n^k(q_j)}{r_j^n} (E_{jkn} \cos k\varphi_j + F_{jkn} \sin k\varphi_j) \end{aligned} \right\} \quad (5.102)$$

$$V_{\theta j} = \left\{ \begin{aligned} & -\frac{k}{r_j^{(n+1)} \sin \theta_j} P_n^k(q_j) (A_{jkn} \sin k\varphi_j - B_{jkn} \cos k\varphi_j) \\ & -\frac{\sin \theta_j}{r_j^{(n+2)}} \frac{dP_n^k(q_j)}{dq_j} (C_{jkn} \cos k\varphi_j + D_{jkn} \sin k\varphi_j) \\ & + \frac{(n-2) \sin \theta_j}{2n\mu(2n-1) r_j^n} \frac{dP_n^k(q_j)}{dq_j} (E_{jkn} \cos k\varphi_j + F_{jkn} \sin k\varphi_j) \end{aligned} \right\} \quad (5.103)$$

$$V_{\varphi j} = \left\{ \begin{aligned} & \frac{\sin \theta_j}{r_j^{(n+1)}} \frac{dP_n^k(q_j)}{dq_j} (A_{jkn} \cos k\varphi_j + B_{jkn} \sin k\varphi_j) \\ & -\frac{k}{r_j^{(n+2)} \sin \theta_j} P_n^k(q_j) (C_{jkn} \sin k\varphi_j - D_{jkn} \cos k\varphi_j) \\ & + \frac{(n-2)k P_n^k(q_j)}{2n\mu(2n-1) r_j^n \sin \theta_j} (E_{jkn} \sin k\varphi_j - F_{jkn} \cos k\varphi_j) \end{aligned} \right\} \quad (5.104)$$

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5.4.2 Analytical modeling

As in the case for the electrical potential, a coordinate transformation between the two spherical coordinate systems $(r_1, \theta_1, \varphi_1)$ and $(r_2, \theta_2, \varphi_2)$ is needed here to express the flow field in a single coordinate system, originating from the center of sphere 1. The algebraic relations between $(r_1, \theta_1, \varphi_1)$ and $(r_2, \theta_2, \varphi_2)$ were provided in equations (5.10) – (5.12). The transformations between the unit vectors in these two coordinate systems are expressed as (Hassonjee et al., 1998),

$$\begin{bmatrix} \hat{\mathbf{e}}_{r2} \\ \hat{\mathbf{e}}_{\theta2} \\ \hat{\mathbf{e}}_{\varphi2} \end{bmatrix} = \begin{bmatrix} f_{121} & f_{221} & f_{321} \\ f_{421} & f_{521} & f_{621} \\ f_{721} & f_{821} & f_{921} \end{bmatrix} \begin{bmatrix} \hat{\mathbf{e}}_{r1} \\ \hat{\mathbf{e}}_{\theta1} \\ \hat{\mathbf{e}}_{\varphi1} \end{bmatrix} \quad (5.105)$$

where

$$\begin{aligned} f_{121} &= \sin \theta_1 \sin \theta_2 \cos(\varphi_2 - \varphi_1) + \cos \theta_1 \cos \theta_2 \\ f_{221} &= \cos \theta_1 \sin \theta_2 \cos(\varphi_2 - \varphi_1) - \sin \theta_1 \cos \theta_2 \\ f_{321} &= \sin \theta_2 \sin(\varphi_2 - \varphi_1) \\ f_{421} &= \sin \theta_1 \cos \theta_2 \cos(\varphi_2 - \varphi_1) - \cos \theta_1 \sin \theta_2 \\ f_{521} &= \cos \theta_1 \cos \theta_2 \cos(\varphi_2 - \varphi_1) + \sin \theta_1 \sin \theta_2 \\ f_{621} &= \cos \theta_2 \sin(\varphi_2 - \varphi_1) \\ f_{721} &= -\sin \theta_1 \sin(\varphi_2 - \varphi_1) \\ f_{821} &= -\cos \theta_1 \sin(\varphi_2 - \varphi_1) \\ f_{921} &= \cos(\varphi_2 - \varphi_1) \end{aligned} \quad (5.106)$$

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The application of the fluid velocity boundary condition on the walls would require that the whole velocity field is transformed to the Cartesian coordinate system (x, y, z) originating from the centre of sphere 1. There are two steps employed in this transformation. Initially, the fluid velocity field is transformed to the spherical coordinate system $(r_1, \theta_1, \varphi_1)$, followed by another transformation of this velocity field into the Cartesian coordinate system. (x, y, z) and $(r_1, \theta_1, \varphi_1)$ coordinate systems are related as

$$x = r_1 \sin \theta_1 \cos \varphi_1, \quad y = r_1 \sin \theta_1 \sin \varphi_1, \quad z = r_1 \cos \theta_1 \quad (5.107)$$

The unite vector transformations between the coordinate systems (x, y, z) and $(r_1, \theta_1, \varphi_1)$, both originating from the centre of sphere 1 is expressed as

$$\begin{bmatrix} \hat{e}_{r_1} \\ \hat{e}_{\theta_1} \\ \hat{e}_{\varphi_1} \end{bmatrix} = \begin{bmatrix} \sin \theta_1 \cos \varphi_1 & \sin \theta_1 \sin \varphi_1 & \cos \theta_1 \\ \cos \theta_1 \cos \varphi_1 & \cos \theta_1 \sin \varphi_1 & -\sin \theta_1 \\ -\sin \varphi_1 & \cos \varphi_1 & 0 \end{bmatrix} \begin{bmatrix} \hat{i} \\ \hat{j} \\ \hat{k} \end{bmatrix} \quad (5.108)$$

$$\begin{aligned} \begin{bmatrix} \hat{i} \\ \hat{j} \\ \hat{k} \end{bmatrix} &= \begin{bmatrix} \sin \theta_1 \cos \varphi_1 & \sin \theta_1 \sin \varphi_1 & \cos \theta_1 \\ \cos \theta_1 \cos \varphi_1 & \cos \theta_1 \sin \varphi_1 & -\sin \theta_1 \\ -\sin \varphi_1 & \cos \varphi_1 & 0 \end{bmatrix}^{-1} \begin{bmatrix} \hat{e}_{r_1} \\ \hat{e}_{\theta_1} \\ \hat{e}_{\varphi_1} \end{bmatrix} \\ &= \begin{bmatrix} \sin \theta_1 \cos \varphi_1 & \cos \theta_1 \cos \varphi_1 & -\sin \varphi_1 \\ \sin \theta_1 \sin \varphi_1 & \cos \theta_1 \sin \varphi_1 & \cos \varphi_1 \\ \cos \theta_1 & -\sin \theta_1 & 0 \end{bmatrix} \begin{bmatrix} \hat{e}_{r_1} \\ \hat{e}_{\theta_1} \\ \hat{e}_{\varphi_1} \end{bmatrix} \end{aligned} \quad (5.109)$$

Hence, the fluid velocity field in terms of $(r_1, \theta_1, \varphi_1)$ can be given as

$$\mathbf{V}_s = \sum_{n=1}^{\infty} \sum_{k=0}^n F_1(r_1, \theta_1, \varphi_1) \hat{e}_{r_1} + F_2(r_1, \theta_1, \varphi_1) \hat{e}_{\theta_1} + F_3(r_1, \theta_1, \varphi_1) \hat{e}_{\varphi_1} \quad (5.110)$$

where

$$F_1(r_1, \theta_1, \varphi_1) = V_{r1} + f_{121}V_{r2} + f_{421}V_{\theta 2} + f_{721}V_{\varphi 2} \quad (5.111)$$

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$$F_2(r_1, \theta_1, \varphi_1) = V_{\theta 1} + f_{221}V_{r2} + f_{521}V_{\theta 2} + f_{821}V_{\varphi 2} \quad (5.112)$$

$$F_3(r_1, \theta_1, \varphi_1) = V_{\varphi 1} + f_{321}V_{r2} + f_{621}V_{\theta 2} + f_{921}V_{\varphi 2} \quad (5.113)$$

The second transformation, i.e., the transformations of V_s onto the Cartesian coordinate system can now be performed to yield an expression for the fluid velocity.

$$\mathbf{V} = \left\{ \begin{aligned} & \left[V_{wx} + \sum_{n=1}^{\infty} \sum_{k=0}^n H_1(x, y, z) \right] \hat{i} + \left[V_{wy} + \sum_{n=1}^{\infty} \sum_{k=0}^n H_2(x, y, z) \right] \hat{j} \\ & + \left[V_{wz} + \sum_{n=1}^{\infty} \sum_{k=0}^n H_3(x, y, z) \right] \hat{k} \end{aligned} \right\} \quad (5.114)$$

where functions H_1 , H_2 and H_3 are expressed as

$$H_1(x, y, z) = H_{11}(x, y, z) + H_{12}(x, y, z) + H_{13}(x, y, z) \quad (5.115)$$

$$H_2(x, y, z) = H_{21}(x, y, z) + H_{22}(x, y, z) + H_{23}(x, y, z) \quad (5.116)$$

$$H_3(x, y, z) = H_{31}(x, y, z) + H_{32}(x, y, z) + H_{33}(x, y, z) \quad (5.117)$$

The analytical expressions for $H_{11}(x, y, z)$ to $H_{33}(x, y, z)$ are lengthy and complicated, and hence, provided in Appendix 2.

Equating (5.94) and (5.114), we get

$$\begin{aligned} V_{x(-b)} &= \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \exp[i(\alpha x + \beta y)] f_{1b}(G_1, G_2, G_3, G'_1, G'_2, G'_3) d\alpha d\beta \\ &+ \sum_{n=1}^{\infty} \sum_{k=0}^n H_1(x, y, b) = \frac{\varepsilon \zeta_w}{\eta} \frac{\partial \phi}{\partial x_{(z=b)}} \end{aligned} \quad (5.118)$$

$$\begin{aligned} V_{x(c)} &= \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \exp[i(\alpha x + \beta y)] f_{1c}(G_1, G_2, G_3, G'_1, G'_2, G'_3) d\alpha d\beta \\ &+ \sum_{n=1}^{\infty} \sum_{k=0}^n H_1(x, y, c) = \frac{\varepsilon \zeta_w}{\eta} \frac{\partial \phi}{\partial x_{(z=c)}} \end{aligned} \quad (5.119)$$

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$$V_{y(-b)} = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \exp[i(\alpha x + \beta y)] i\beta f_{2b}(G_1, G_2, G_3, G_1', G_2', G_3') d\alpha d\beta$$

$$+ \sum_{n=1}^{\infty} \sum_{k=0}^n H_2(x, y, -b) = \frac{\varepsilon \zeta_w}{\eta} \frac{\partial \phi}{\partial y_{(z=b)}} \quad (5.120)$$

$$V_{y(c)} = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \exp[i(\alpha x + \beta y)] i\beta f_{2c}(G_1, G_2, G_3, G_1', G_2', G_3') d\alpha d\beta$$

$$+ \sum_{n=1}^{\infty} \sum_{k=0}^n H_2(x, y, c) = \frac{\varepsilon \zeta_w}{\eta} \frac{\partial \phi}{\partial y_{(z=c)}} \quad (5.121)$$

$$V_{z(-b)} = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \exp[i(\alpha x + \beta y)] f_{3b}(G_1, G_2, G_3, G_1', G_2', G_3') d\alpha d\beta$$

$$+ \sum_{n=1}^{\infty} \sum_{k=0}^n H_3(x, y, -b) = \frac{\varepsilon \zeta_w}{\eta} \frac{\partial \phi}{\partial z_{(z=b)}} = 0 \quad (5.122)$$

$$V_{z(c)} = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \exp[i(\alpha x + \beta y)] f_{3c}(G_1, G_2, G_3, G_1', G_2', G_3') d\alpha d\beta$$

$$+ \sum_{n=1}^{\infty} \sum_{k=0}^n H_3(x, y, c) = \frac{\varepsilon \zeta_w}{\eta} \frac{\partial \phi}{\partial z_{(z=c)}} = 0 \quad (5.123)$$

where

$$f_{1b}(G_1, G_2, G_3, G_1', G_2', G_3') = \left\{ \begin{aligned} &\exp(\kappa b) \left[\frac{i\alpha}{\kappa} G_1 + \frac{2}{\kappa} G_2 - \frac{\alpha^2}{\kappa^3} (1 - \kappa b) G_2 - \frac{b\alpha^2}{\kappa} G_3 \right] \\ &+ \exp(-\kappa b) \left[\frac{i\alpha}{\kappa} G_1' + \frac{2}{\kappa} G_2' - \frac{\alpha^2}{\kappa^3} (1 + \kappa b) G_2' - \frac{b\alpha^2}{\kappa} G_3' \right] \end{aligned} \right\} \quad (5.124)$$

$$f_{1c}(G_1, G_2, G_3, G_1', G_2', G_3') = \left\{ \begin{aligned} &\exp(-\kappa c) \left[\frac{i\alpha}{\kappa} G_1 + \frac{2}{\kappa} G_2 - \frac{\alpha^2}{\kappa^3} (1 + \kappa c) G_2 + \frac{c\alpha^2}{\kappa} G_3 \right] \\ &+ \exp(\kappa c) \left[\frac{i\alpha}{\kappa} G_1' + \frac{2}{\kappa} G_2' - \frac{\alpha^2}{\kappa^3} (1 - \kappa c) G_2' + \frac{c\alpha^2}{\kappa} G_3' \right] \end{aligned} \right\} \quad (5.125)$$

$$f_{2b}(G_1, G_2, G_3, G_1', G_2', G_3') = \left\{ \begin{aligned} &\exp(\kappa b) \left[\frac{G_1}{\kappa} + \frac{i\alpha}{\kappa^3} G_2 (1 - \kappa b) + \frac{i\alpha b}{\kappa} G_3 \right] \\ &+ \exp(-\kappa b) \left[\frac{G_1'}{\kappa} + \frac{i\alpha}{\kappa^3} G_2' (1 + \kappa b) + \frac{i\alpha b}{\kappa} G_3' \right] \end{aligned} \right\} \quad (5.126)$$

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$$f_{2c} \begin{pmatrix} G_1, G_2, G_3, \\ G'_1, G'_2, G'_3 \end{pmatrix} = \left\{ \begin{aligned} &\exp(-\kappa c) \left[\frac{G_1}{\kappa} + \frac{i\alpha}{\kappa^3} G_2 (1 + \kappa c) - \frac{i\alpha c}{\kappa} G_3 \right] \\ &+ \exp(\kappa c) \left[\frac{G'_1}{\kappa} + \frac{i\alpha}{\kappa^3} G'_2 (1 - \kappa c) - \frac{i\alpha c}{\kappa} G'_3 \right] \end{aligned} \right\} \quad (5.127)$$

$$f_{3b} \begin{pmatrix} G_1, G_2, G_3, \\ G'_1, G'_2, G'_3 \end{pmatrix} = \left\{ \begin{aligned} &\exp(\kappa b) \left[-G_1 - \frac{i\alpha b}{\kappa} G_2 + \frac{i\alpha}{\kappa} (1 - \kappa b) G_3 \right] \\ &+ \exp(-\kappa b) \left[G'_1 - \frac{bi\alpha}{\kappa} G'_2 + \frac{i\alpha}{\kappa} (1 + \kappa b) G'_3 \right] \end{aligned} \right\} \quad (5.128)$$

$$f_{3c} \begin{pmatrix} G_1, G_2, G_3, \\ G'_1, G'_2, G'_3 \end{pmatrix} = \left\{ \begin{aligned} &\exp(-\kappa c) \left[-G_1 - \frac{i\alpha c}{\kappa} G_2 + \frac{i\alpha}{\kappa} (1 + \kappa c) G_3 \right] \\ &+ \exp(\kappa c) \left[G'_1 - \frac{ci\alpha}{\kappa} G'_2 + \frac{i\alpha}{\kappa} (1 - \kappa c) G'_3 \right] \end{aligned} \right\} \quad (5.129)$$

Utilization of Fourier transforms on the variables x and y in equations (5.118) to (5.123), lead to a solution of functions $G_1 - G'_3$ in terms of the coefficients $A_{jkn} - F_{jkn}$. The resulting equations can be expressed in matrix form as,

$$\begin{bmatrix} a_{11} & a_{12} & a_{13} & a_{14} & a_{15} & a_{16} \\ a_{21} & a_{22} & a_{23} & a_{24} & a_{25} & a_{26} \\ a_{31} & a_{32} & a_{33} & a_{34} & a_{35} & a_{36} \\ a_{41} & a_{42} & a_{43} & a_{44} & a_{45} & a_{46} \\ a_{51} & a_{52} & a_{53} & a_{54} & a_{55} & a_{56} \\ a_{61} & a_{62} & a_{63} & a_{64} & a_{65} & a_{66} \end{bmatrix} \begin{bmatrix} G_1 \\ G_2 \\ G_3 \\ G'_1 \\ G'_2 \\ G'_3 \end{bmatrix} = \begin{bmatrix} d_1 \\ d_2 \\ d_3 \\ d_4 \\ d_5 \\ d_6 \end{bmatrix} \quad (5.130)$$

where the matrix coefficients are expressed as

$$\begin{aligned} a_{11} &= \exp(\kappa b) \frac{i\alpha}{\kappa}, \quad a_{12} = \exp(\kappa b) \left(\frac{2}{\kappa} - \frac{\alpha^2}{\kappa^3} (1 - \kappa b) \right), \quad a_{13} = -\exp(\kappa b) \left(\frac{b\alpha^2}{\kappa} \right) \\ a_{14} &= \exp(-\kappa b) \frac{i\alpha}{\kappa}, \quad a_{15} = \exp(-\kappa b) \left[\frac{2}{\kappa} - \frac{(1 + \kappa b)\alpha^2}{\kappa^3} \right], \quad a_{16} = \exp(-\kappa b) \left(\frac{b\alpha^2}{\kappa} \right) \\ a_{21} &= \exp(-\kappa c) \frac{i\alpha}{\kappa}, \quad a_{22} = \exp(-\kappa c) \left(\frac{2}{\kappa} - \frac{\alpha^2}{\kappa^3} (1 + \kappa c) \right), \quad a_{23} = \exp(-\kappa c) \left(\frac{c\alpha^2}{\kappa} \right) \end{aligned}$$

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$$\begin{aligned}
a_{24} &= \exp(\kappa c) \frac{i\alpha}{\kappa}, \quad a_{25} = \exp(\kappa c) \left[\frac{2}{\kappa} - \frac{(1-\kappa c)\alpha^2}{\kappa^3} \right], \quad a_{26} = -\exp(\kappa c) \left(\frac{c\alpha^2}{\kappa} \right) \\
a_{31} &= \frac{\exp(\kappa b)}{\kappa} i\beta, \quad a_{32} = \frac{\alpha\beta}{\kappa^3} (1-\kappa b) \exp(\kappa b), \quad a_{33} = \frac{\alpha\beta b}{\kappa} \exp(\kappa b) \\
a_{34} &= \frac{\exp(-\kappa b)}{\kappa} i\beta, \quad a_{35} = -\frac{\alpha\beta}{\kappa^3} (1+\kappa b) \exp(-\kappa b), \quad a_{36} = -\frac{\alpha\beta b}{\kappa} \exp(-\kappa b) \\
a_{41} &= \frac{\exp(-\kappa c)}{\kappa} i\beta, \quad a_{42} = \frac{\alpha\beta}{\kappa^3} (1+\kappa c) \exp(-\kappa c), \quad a_{43} = \frac{\alpha\beta c}{\kappa} \exp(-\kappa c) \\
a_{44} &= \frac{\exp(\kappa c)}{\kappa} i\beta, \quad a_{45} = -\frac{\alpha\beta}{\kappa^3} (1-\kappa c) \exp(\kappa c), \quad a_{46} = \frac{\alpha\beta c}{\kappa} \exp(\kappa c) \\
a_{51} &= -\exp(\kappa b), \quad a_{52} = \frac{i\alpha b}{\kappa} \exp(\kappa b), \quad a_{53} = \frac{i\alpha}{\kappa} (1-\kappa b) \exp(\kappa b) \\
a_{54} &= \exp(-\kappa b), \quad a_{55} = \frac{bi\alpha}{\kappa} \exp(-\kappa b), \quad a_{56} = \frac{i\alpha}{\kappa} (1+\kappa b) \exp(-\kappa b) \\
a_{61} &= -\exp(-\kappa c), \quad a_{62} = \frac{-i\alpha c}{\kappa} \exp(-\kappa c), \quad a_{63} = \frac{i\alpha}{\kappa} (1+\kappa c) \exp(-\kappa c) \\
a_{64} &= \exp(\kappa c), \quad a_{65} = -\frac{ci\alpha}{\kappa} \exp(\kappa c), \quad a_{66} = \frac{i\alpha}{\kappa} (1-\kappa c) \exp(\kappa c)
\end{aligned} \tag{5.131}$$

Integral functions $d_1 - d_6$ present in the right hand side matrix in equation (5.130) are in turn expressed as

$$d_1 = \frac{1}{2\pi} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \left[\frac{\varepsilon \zeta_w}{\eta} \frac{\partial \phi}{\partial x} \Big|_{(z=-b)} - \sum_{n=1}^{\infty} \sum_{k=0}^n H_1(x, y, -b) \right] \exp[-i(\alpha x + \beta y)] dx dy \tag{5.132}$$

$$d_2 = \frac{1}{2\pi} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \left[\frac{\varepsilon \zeta_w}{\eta} \frac{\partial \phi}{\partial x} \Big|_{(z=c)} - \sum_{n=1}^{\infty} \sum_{k=0}^n H_1(x, y, c) \right] \exp[-i(\alpha x + \beta y)] dx dy \tag{5.133}$$

$$d_3 = \frac{1}{2\pi} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \left[\frac{\varepsilon \zeta_w}{\eta} \frac{\partial \phi}{\partial y} \Big|_{(z=-b)} - \sum_{n=1}^{\infty} \sum_{k=0}^n H_2(x, y, -b) \right] \exp[-i(\alpha x + \beta y)] dx dy \tag{5.134}$$

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$$d_4 = \frac{1}{2\pi} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \left[\frac{\varepsilon \zeta_w}{\eta} \frac{\partial \phi}{\partial y_{(z=c)}} - \sum_{n=1}^{\infty} \sum_{k=0}^n H_2(x, y, c) \right] \exp[-i(\alpha x + \beta y)] dx dy \quad (5.135)$$

$$d_5 = -\frac{1}{2\pi} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \left[\sum_{n=1}^{\infty} \sum_{k=0}^n H_3(x, y, -b) \right] \exp[-i(\alpha x + \beta y)] dx dy \quad (5.136)$$

$$d_6 = -\frac{1}{2\pi} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \left[\sum_{n=1}^{\infty} \sum_{k=0}^n H_3(x, y, c) \right] \exp[-i(\alpha x + \beta y)] dx dy \quad (5.137)$$

Again, integrals $d_1 - d_6$ are transformed using the Hankel transform technique described in section 5.3.2.1. Equation (5.129) can then be solved for the functions $G_1 - G_3'$.

In order to apply the boundary conditions on the sphere surfaces, the whole velocity field should be expressed in spherical coordinates originating from the centre of sphere 1 and sphere 2. Employing the Cartesian-to-spherical coordinate transformation expressed by equation (5.107) – (5.109), the velocity field can be written in terms of the spherical coordinate system from the centre of sphere 1,

$$\mathbf{V} = V_r \hat{\mathbf{e}}_{r1} + V_\theta \hat{\mathbf{e}}_{\theta1} + V_\phi \hat{\mathbf{e}}_{\phi1} \quad (5.138)$$

$$V_r = \left\{ \begin{aligned} & \sin \theta_1 \cos \phi_1 \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \exp[i(\alpha x + \beta y)] f_{1z} (G_1, G_2, G_3, G_1', G_2', G_3') d\alpha d\beta \\ & + \sin \theta_1 \sin \phi_1 \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \exp[i(\alpha x + \beta y)] i\beta f_{2z} (G_1, G_2, G_3, G_1', G_2', G_3') d\alpha d\beta \\ & \cos \theta_1 \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \exp[i(\alpha x + \beta y)] i\beta f_{3z} (G_1, G_2, G_3, G_1', G_2', G_3') d\alpha d\beta \\ & + \sum_{n=1}^{\infty} \sum_{k=0}^n F_1(r_1, \theta_1, \phi_1) \end{aligned} \right\} \quad (5.139)$$

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$$V_{\theta} = \left\{ \begin{aligned} & \cos \theta_1 \cos \varphi_1 \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \exp[i(\alpha x + \beta y)] f_{1z}(G_1, G_2, G_3, G'_1, G'_2, G'_3) d\alpha d\beta \\ & + \cos \theta_1 \sin \varphi_1 \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \exp[i(\alpha x + \beta y)] i\beta f_{2z}(G_1, G_2, G_3, G'_1, G'_2, G'_3) d\alpha d\beta \\ & - \sin \theta_1 \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \exp[i(\alpha x + \beta y)] i\beta f_{3z}(G_1, G_2, G_3, G'_1, G'_2, G'_3) d\alpha d\beta \\ & + \sum_{n=1}^{\infty} \sum_{k=0}^n F_2(r_1, \theta_1, \varphi_1) \end{aligned} \right\} \quad (5.140)$$

$$V_{\varphi} = \left\{ \begin{aligned} & -\sin \varphi_1 \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \exp[i(\alpha x + \beta y)] f_{1z}(G_1, G_2, G_3, G'_1, G'_2, G'_3) d\alpha d\beta \\ & \cos \varphi_1 \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \exp[i(\alpha x + \beta y)] i\beta f_{2z}(G_1, G_2, G_3, G'_1, G'_2, G'_3) d\alpha d\beta \\ & + \sum_{n=1}^{\infty} \sum_{k=0}^n F_3(r_1, \theta_1, \varphi_1) \end{aligned} \right\} \quad (5.141)$$

Similarly, in order to apply boundary condition on the surface of particle 2, the whole velocity field should be expressed in spherical coordinate system form the center of sphere 2. This is achieved through the following transformations.

$$V = \sum_{n=1}^{\infty} \sum_{k=0}^n F'_1(r_2, \theta_2, \varphi_2) \hat{e}_{r2} + F'_2(r_2, \theta_2, \varphi_2) \hat{e}_{\theta2} + F'_3(r_2, \theta_2, \varphi_2) \hat{e}_{\varphi2} \quad (5.142)$$

where

$$F'_1(r_2, \theta_2, \varphi_2) = V_{r2} + f_{112} V_{r1} + f_{412} V_{\theta1} + f_{712} V_{\varphi1} \quad (5.143)$$

$$F'_2(r_2, \theta_2, \varphi_2) = V_{\theta2} + f_{212} V_{r1} + f_{512} V_{\theta1} + f_{812} V_{\varphi1} \quad (5.144)$$

$$F'_3(r_2, \theta_2, \varphi_2) = V_{\varphi2} + f_{312} V_{r1} + f_{612} V_{\theta1} + f_{912} V_{\varphi1} \quad (5.145)$$

The unit vectors in the two spherical coordinate systems are related by the expression,

$$\begin{bmatrix} \hat{e}_{r1} \\ \hat{e}_{\theta1} \\ \hat{e}_{\varphi1} \end{bmatrix} = \begin{bmatrix} f_{112} & f_{212} & f_{312} \\ f_{412} & f_{512} & f_{612} \\ f_{712} & f_{812} & f_{912} \end{bmatrix} \begin{bmatrix} \hat{e}_{r2} \\ \hat{e}_{\theta2} \\ \hat{e}_{\varphi2} \end{bmatrix} \quad (5.146)$$

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where

$$\begin{aligned}
 f_{112} &= \sin \theta_1 \sin \theta_2 \cos(\varphi_2 - \varphi_1) + \cos \theta_1 \cos \theta_2 \\
 f_{212} &= \sin \theta_1 \cos \theta_2 \cos(\varphi_2 - \varphi_1) - \cos \theta_1 \sin \theta_2 \\
 f_{312} &= -\sin \theta_1 \sin(\varphi_2 - \varphi_1) \\
 f_{412} &= \cos \theta_1 \sin \theta_2 \cos(\varphi_2 - \varphi_1) - \sin \theta_1 \cos \theta_2 \\
 f_{512} &= \cos \theta_1 \cos \theta_2 \cos(\varphi_2 - \varphi_1) + \sin \theta_1 \sin \theta_2 \\
 f_{612} &= -\cos \theta_1 \sin(\varphi_2 - \varphi_1) \\
 f_{712} &= \sin \theta_2 \sin(\varphi_2 - \varphi_1) \\
 f_{812} &= \cos \theta_2 \sin(\varphi_2 - \varphi_1) \\
 f_{912} &= \cos(\varphi_2 - \varphi_1)
 \end{aligned} \tag{5.147}$$

Hence,

$$V = V'_r \hat{e}_{r2} + V'_\theta \hat{e}_{\theta2} + V'_\varphi \hat{e}_{\varphi2}$$

In the above equations, V'_r , V'_θ and V'_φ are expressed as

$$V'_r = \left\{ \begin{aligned} & \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \exp[i(\alpha x + \beta y)] f_{1z}(G_1, G_2, G_3, G'_1, G'_2, G'_3) d\alpha d\beta \\ & (f_{112} \sin \theta_1 \cos \varphi_1 + f_{412} \cos \theta_1 \cos \varphi_1 - f_{712} \sin \varphi_1) \\ & \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \exp[i(\alpha x + \beta y)] i\beta f_{2z}(G_1, G_2, G_3, G'_1, G'_2, G'_3) d\alpha d\beta \\ & (f_{112} \sin \theta_1 \sin \varphi_1 + f_{412} \cos \theta_1 \sin \varphi_1 + f_{712} \cos \varphi_1) \\ & \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \exp[i(\alpha x + \beta y)] i\beta f_{3z}(G_1, G_2, G_3, G'_1, G'_2, G'_3) d\alpha d\beta \\ & (f_{112} \cos \theta_1 - f_{412} \sin \theta_1) + \sum_{n=1}^{\infty} \sum_{k=0}^n F'_1(r_2, \theta_2, \varphi_2) \end{aligned} \right\} \tag{5.148}$$

$$V_{\theta}' = \left\{ \begin{array}{l} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \exp[i(\alpha x + \beta y)] f_{1z}(G_1, G_2, G_3, G_1', G_2', G_3') d\alpha d\beta \\ (f_{212} \sin \theta_1 \cos \varphi_1 + f_{512} \cos \theta_1 \cos \varphi_1 - f_{812} \sin \varphi_1) \\ \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \exp[i(\alpha x + \beta y)] i\beta f_{2z}(G_1, G_2, G_3, G_1', G_2', G_3') d\alpha d\beta \\ (f_{212} \sin \theta_1 \sin \varphi_1 + f_{512} \cos \theta_1 \sin \varphi_1 + f_{812} \cos \varphi_1) \\ \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \exp[i(\alpha x + \beta y)] i\beta f_{3z}(G_1, G_2, G_3, G_1', G_2', G_3') d\alpha d\beta \\ (f_{212} \cos \theta_1 - f_{512} \sin \theta_1) + \sum_{n=1}^{\infty} \sum_{k=0}^n F_2'(r_2, \theta_2, \varphi_2) \end{array} \right\} \quad (5.149)$$

$$V_{\varphi}' = \left\{ \begin{array}{l} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \exp[i(\alpha x + \beta y)] f_{1z}(G_1, G_2, G_3, G_1', G_2', G_3') d\alpha d\beta \\ (f_{312} \sin \theta_1 \cos \varphi_1 + f_{612} \cos \theta_1 \cos \varphi_1 - f_{912} \sin \varphi_1) \\ \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \exp[i(\alpha x + \beta y)] i\beta f_{2z}(G_1, G_2, G_3, G_1', G_2', G_3') d\alpha d\beta \\ (f_{312} \sin \theta_1 \sin \varphi_1 + f_{612} \cos \theta_1 \sin \varphi_1 + f_{912} \cos \varphi_1) \\ \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \exp[i(\alpha x + \beta y)] i\beta f_{3z}(G_1, G_2, G_3, G_1', G_2', G_3') d\alpha d\beta \\ (f_{312} \cos \theta_1 - f_{612} \sin \theta_1) + \sum_{n=1}^{\infty} \sum_{k=0}^n F_3'(r_2, \theta_2, \varphi_2) \end{array} \right\} \quad (5.150)$$

5.4.3 Boundary collocation and evaluation of particle velocity

To satisfy the boundary condition on the entire surface of the sphere would require the solution of the entire infinite array of unknown constants $A_{jkn} \rightarrow F_{jkn}$. However, the boundary collocation technique (Ganatos et al., 1990) is based on the truncation of this infinite series, and for the case of two spheres moving in the same plane (x - z plane, in the present study), the boundary conditions can be enforced on a finite number of points on the generating circular arc (from $\theta_1, \theta_2 = 0$ to π). If the infinite series in equation is

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truncated after $k = K$ and $n = N$ terms, equations (5.87) and (5.88) represent $6KN$ linear algebraic equations through which the functions $A_{jkn} \rightarrow F_{jkn}$ and the unknown particle velocities (U_1, ω_1 and U_2, ω_2) are related.

Because the surface of each sphere encompasses a neutral body, the net drag force and torque exerted by the fluid on the particle must be zero (Keh et al. 1993). The hydrodynamic force and torque acting on the i^{th} sphere is expressed as (Happel and Brenner, 1973)

$$\mathbf{F}_i = -4\pi\nabla(r_j^3 P_{-2,j}) \quad (5.151)$$

$$\mathbf{T}_i = -8\pi\nabla(r_j^3 \chi_{-2,j}) \quad (5.152)$$

Using equation (5.100), the Cartesian components of the force and torque exerted by the fluid on the i^{th} sphere can be expressed as

$$\mathbf{F}_i = -4\pi[E_{i11}\mathbf{i} + F_{i11}\mathbf{j} + E_{i01}\mathbf{k}] \quad (5.153)$$

$$\mathbf{T}_i = -8\pi\eta[A_{i11}\mathbf{i} + B_{i11}\mathbf{j} + A_{i01}\mathbf{k}] \quad (5.154)$$

From the above equations, it is apparent that

$$A_{i01} = 0, A_{i11} = 0, B_{i11} = 0, E_{i01} = 0, E_{i11} = 0 \text{ and } F_{i11} = 0 \quad (5.155)$$

Now, $\mathbf{F}_i$ and $\mathbf{T}_i$ can be equated to zero, and this results in 12 simultaneous equations for the evaluation of 12 unknowns that represent the translational and rotational velocities of the two spheres. Once, the particle velocities are obtained, the particle trajectories are calculated via the simple Euler algorithm,

$$\mathbf{r}(t + \Delta t) = \mathbf{r}(t) + \mathbf{U}_p \Delta t \quad (5.156)$$

where $\mathbf{U}_p$ is the particle velocity and $\mathbf{r}(t)$ represents the particle position at time t .

5.5 Results and discussion

5.5.1 Axisymmetric motion of a sphere in a microchannel – Literature comparison

Fig 5.2 Normalized electrophoretic velocity of a sphere in a parallel plate microchannel as a function of the separation parameter a/b .

Fig 5.2 shows the normalized particle velocity U/U_s of a spherical particle undergoing electrophoresis in the median plane parallel to two plane walls as a function of the ratio of particle radius to half channel depth (separation parameter), a/b . Here, U_s refers to the velocity of the particle in the bulk fluid, defined by

$$U_s = \frac{\varepsilon_0 \varepsilon_r (\zeta_p - \zeta_w) E_\infty}{\mu} \quad (5.157)$$

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The solid lines represent the boundary collocation results; whereas the dotted lines represent the results from Keh et al. (1985) calculated using the method of reflections, and boundary collocation results from Keh et al. (2002b). The reflection results are in good agreement with the collocation results until $a/b \leq 0.7$. But the asymptotic formula given by the method of reflections is in error, especially when $\lambda > 0.9$. In the region $0.7 \leq a/b \leq 0.9$, these results seem to slightly overestimate the collocation results. The theoretical results from the study matches well with the collocation results from the literature.

5.5.2 Eccentric motion of a sphere in a microchannel

Fig 5.3 Plots of the normalized translational velocity of a sphere undergoing electrophoresis parallel to two plane walls versus the ratio $b/(b+c)$ with a/b and $2a/(b+c)$ as parameters.

Fig 5.4 Plots of the normalized rotational velocity of a sphere undergoing electrophoresis parallel to two plane walls versus the ratio $b/(b+c)$ with a/b and $2a/(b+c)$ as parameters.

In this section, the translational and rotational motion of a sphere moving between two parallel plates at an arbitrary distance between them is discussed. The normalized translational velocity, U/U_s is plotted as a function of $b/(b+c)$ for various values of a/b and $2a/(b+c)$ in Fig 5.3. The dotted lines illustrate the effect of the second wall ($z=c$) on the particle velocities for various values of the relative sphere-to-first wall spacing, a/b . The solid lines illustrate the effect of the sphere position at various values of the relative wall to wall spacing, $2a/(b+c)$. It can be observed that the effect of the second wall is to reduce the particle mobility until $a/b=0.8$. However, for much closer

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separations between the particle and the first wall, the particle mobility is reduced initially, but a dramatic increase is followed when $b/(b+c) > 0.45$. This effect can be attributed to the increase in electrical stresses in the fluid in the narrow gap between the particle and the wall, which causes an increase in the driving force on the particle. Also, the effect of the second wall becomes stronger as a/b increases. At a given value of $2a/(b+c)$, the particle experiences maximum viscous drag and has minimum velocity when it is located midway between the walls. Also, the eccentricity of particle motion increases its velocity. In Fig 5.4, dimensionless particle rotational velocity $-a_p \omega / U_s$ is plotted as a function of $b/(b+c)$ for various values of a/b and $2a/(b+c)$. The presence of the upper wall decreases the particle rotational velocity, and the influence of the upper wall becomes stronger as a/b increases. As $b/(b+c) = 0.5$ (the particle is evenly placed between the walls), $\omega = 0$. Also, the eccentricity of particle motion increases the its rotational velocity.

5.5.3 Asymmetric motion of two spheres in a parallel plate microchannel

5.5.3.1. Effect of particle spacing ratio, γ

Fig 5.5(a) shows the effect of the ratio of particle diameter to channel depth ($\gamma = 2a_p/(b+c)$) on the trajectories of a charged colloidal particle moving in the vicinity of an attached particle located at $X^* = 10$ ($X^* = x/a_p$) in a parallel plate microchannel. The plotted curves show the trajectories for three different γ ratios, 0.1, 0.2 and 0.4, for $E_\infty = 10^4 V/m$.

Fig 5.5(a) Effect of particle size ratio, γ on the Trajectories of a particle in the vicinity of an attached particle located at $X^* = 10$. $E = 10^4 V/m$. Other calculation parameters include, $\zeta_{p1}/\zeta_w = \zeta_{p2}/\zeta_w = 2$, $a_2/a_1 = 1$.

Fig 5.5(b) Effect of particle size ratio, γ on the X- velocity of the particle, U_x/U_s of a particle in the vicinity of an attached particle located at $X^* = 10$. Other calculation parameters include, $E = 10^4 V/m$, $\zeta_{p1}/\zeta_w = \zeta_{p2}/\zeta_w = 2$, $a_2/a_1 = 1$.

Fig 5.5(c) Effect of particle size ratio, γ on the Z - velocity of a particle moving in the vicinity of an attached particle located at $X^* = 10$. Other calculation parameters include, $E = 10^4 V/m$, $\zeta_{p1} / \zeta_w = \zeta_{p2} / \zeta_w = 2$, $a_2 / a_1 = 1$.

It is observed that the deviation of the moving particle in the neighborhood of the attached particle increases as the γ ratio is increased. This implies that the velocity of the particle increases in the vicinity of the attached particle, as the spacing ratio is increased. In order to explain this effect, the plots of the particle velocities (dimensionless) U_x / U_s and U_z / U_s for the same case are presented in Fig 5.5(b) and Fig 5.5(c), respectively. In the vicinity of the attached particle, the x - directional velocity of the particle decreases

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until $\gamma = 0.3$, owing to the increased hydrodynamic drag exerted on the moving particle. However, for the cases of $\gamma = 0.35$ and 0.4 the particle velocity surprisingly increases. An explanation for this effect can be provided as follows: as the moving particle approaches the attached particle the driving force on the particle increases due to the strong deformation of the electric field in the narrow gap between the two particles, speeding up the particle. When the spacing becomes sufficiently large ($\gamma = 0.35, 0.4$), the effect due to hydrodynamic drag is overcome by the driving force on the particle and U_x increases. 12 % increase in particle velocity is observed as $\gamma = 0.4$. However, U_z increases in the vicinity of the attached particle for whole range of spacing ratios studied. This can be attributed to the combined effect of hydrodynamic interactions (which act in the positive z direction when the moving particle approaches the attached particle) and the increase in electrokinetic driving force due to the abovementioned reason. In general, it can be inferred that, for the same channel size, larger particles in the vicinity of similarly sized particles can travel faster, if the spacing ratio become sufficiently large.

5.5.3.2 Effect of electric field strength

Fig 5.6 shows the effect of electric field strength on the trajectories of a colloidal particle in the vicinity of a neighboring particle of similar size in a microchannel. The position of the fixed particle, $X^* = 10$, and the spacing ratio $\gamma = 0.4$. All other calculation parameters remain the same as used for plotting Fig 5.5(a) (zeta potential ratio and particle radius ratio).

Fig 5.6 Effect of applied electric field strength on the trajectories of a particle in the vicinity of an attached particle located at $X^* = 10$. Other calculation parameters include, $\zeta_{p1} / \zeta_w = \zeta_{p2} / \zeta_w = 2$, $a_2 / a_1 = 1$, $\gamma = 0.4$.

It can be observed that the deviation of the moving particle in the vicinity of the attached particle becomes stronger with an increase in the applied field strength. With the geometric parameters such as γ and a_2 / a_1 remain the same in all the three cases, this effect implies an increase in driving force on the particle, resulted from a strong deformation of the electric field surrounding the moving particle. The gradient of electrical potential, $\nabla\phi$, depends on the field strength, E_∞ , and as a result, larger changes in electrical potential are brought about with increase in the field strength as the particle

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passes through the narrow gap between the fixed particle and the wall. Hence, an increase in electrical potential gradient in the z -direction ($\partial\phi/\partial z$) causes an increase in the z -directional velocity of the moving particle and this results in the deviation of the moving particle in the vicinity of the attached particle.

5.5.3.3 Effect of particle separation

Fig 5.7 Effect of particle-wall separation on the trajectories of a particle in the vicinity of an attached particle located at $X^* = 10$. Other calculation parameters include, $E = 10^4 V/m$, $\zeta_{p1}/\zeta_w = \zeta_{p2}/\zeta_w = 2$, $a_2/a_1 = 1$, $\gamma = 0.4$.

The effect of particle-wall separation on particle transport is shown in Fig 5.7. The trajectories of a particle are plotted for various values of initial particle-wall separation

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distance (dimensionless), z^* ($z^* = z / a_p$). The geometric parameters, $a_2 / a_1 = 1$ and $\gamma = 0.4$. In another words, this figure shows the effect of interparticle separation distance on particle transport. Comparing the initial and final position of the moving particle from the figure, it can be noticed that the difference in particle-wall separation in the three cases (represented by $z^* = 3$, $z^* = 2.8$ and $z^* = 2.6$) are reduced once the moving particle traverse past the fixed particle. This implies a stronger deformation of the electric field surrounding the moving particle in the vicinity of the fixed particle, causing an increase in the electrokinetic driving force on the particle. This result shows that, interparticle separation can play a predominant role in particle separation in microfluidic devices.

5.5.4 Relative motion of two spheres in a parallel plate microchannel

5.5.4.1 Effect of particle size

This section deals with the discussion of the relative motion of two spheres in a parallel plate microchannel. The reactive trajectories of two spheres of different size are plotted for $E_\infty = 10^4 V / m$. The other calculation parameters are $\zeta_{p1} / \zeta_w = \zeta_{p2} / \zeta_w = 2$, $a_2 / a_1 = 2$ and $\gamma_1 = 0.2$ where $\gamma_1 = 2a_1 / (b + c)$. Here, γ_1 represents the spacing ratio of the first particle in the microchannel. It is observed that the particle motion is dependent on its size. A smaller particle moves faster, and overtakes a larger particle moving in front, when the centres of the spheres are not located on the same line parallel to the applied electric field. This result can be explained from the fact that, there is an increase in electrical stresses in the narrow gap between the two spheres on approach. Hence, there is an increase in the electrokinetic driving force in the vicinity of the particles. Also, it has to be mentioned here that, in the case shown in Fig 5.8(a), the Z- component of

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hydrodynamic force on sphere 1 acts in the +ve z -direction whereas on sphere 2, Z component of hydrodynamic force is directed in the -ve z -direction. Fig 5.8(b) and 5.8(c) shows the dimensionless x -velocity and z -velocity of particle 1 and 2, respectively. It is noted that the increase in translational velocity (in x and z directions) of particle 1 is significantly larger compared to the second sphere. Hence, the smaller particle climbs over the larger particle, while the larger particle is pushed down slightly during the transport.

Fig 5.8(a) Trajectories of two spheres of different size undergoing relative motion in a microchannel. Other parameters used for calculation include $\zeta_{p1}/\zeta_w = \zeta_{p2}/\zeta_w = 2$, $a_2/a_1 = 2$, $\gamma_1 = 0.2$, and $E = 10^4 V/m$.

Fig 5.8(b) Dimensionless X - velocity of particle 1 and 2 for the case plotted in Fig 5.8(a). Other parameters used for calculation include $\zeta_{p1} / \zeta_w = \zeta_{p2} / \zeta_w = 2$, $a_2 / a_1 = 2$, $\gamma_1 = 0.2$, and $E = 10^4 V/m$.

Fig 5.8(c) Dimensionless Z- velocity of particle 1 and 2 for the case plotted in Fig 5.8(a). Other parameters used for calculation include $\zeta_{p1}/\zeta_w = \zeta_{p2}/\zeta_w = 2$, $a_2/a_1 = 2$, $\gamma_1 = 0.2$, and $E = 10^4 V/m$.

5.5.4.2 Effect of particle zeta potential ratio

The zeta potentials of the channel wall and the particles are critical for the electroosmosis and electrophoresis. The particle motion is the result of the electrophoretic motion coupled with the electroosmotic flow field in the channel. Fig 5.9 shows the effect of particle zeta potential on the relative motion of two equally sized spheres in a microchannel. The trajectories of two spheres with zeta potential ratios (represented by ζ_{p1}/ζ_{p2}) 1.5 and 2 are plotted where the particle-wall zeta potential ratio for the first particle, $\zeta_{p1}/\zeta_w = 2$. Hence, in this case, the electrophoretic mobility of the particles is

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larger than the electroosmotic mobility. Fig 5.9 indicate that, particles with larger zeta potential can override particle with smaller zeta potentials moving in front, when the centers of the spheres are not located along the same line parallel to the applied field. Particle 1 climbs over particle 2 due to the combined effect of hydrodynamic and electrokinetic interactions that enhance the particle velocity. This implies that, in microfluidic devices, particle separation can be achieved based on their zeta potential.

Fig 5.9 Effect of particle zeta potential on the relative motion of two equally sized spheres in a microchannel. Other parameters used for calculation include $\zeta_{p1}/\zeta_w = 2$, $a_2/a_1 = 1$, $\gamma_1 = 0.2$, and $E = 10^4 V/m$.

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an increase in the driving force on particle 2 and thereby speeding up the particle. However, in the second case, the electrohydrodynamic interactions between the particles overcome the effect due to the distortion of electric field in the vicinity of particle 2 and channel wall. Hence, particle 1 climbs over particle 2 and travels faster.

5.6 Summary

An analytical model for investigating the electrophoretic motion of two spheres in a parallel plate microchannel is developed in this chapter. The solutions of Laplace equation governing the electrical potential and Stokes equation for the flow field are formulated analytically. This is performed by an analytical inversion of the Fourier transform of wall disturbances (expressed by Fourier integrals) to satisfy the boundary conditions on the surface of the spheres, where the disturbance due to the spheres are represented by spherical harmonic functions. The analytical results for the case of axisymmetric motion of a single sphere in a parallel plate microchannel are validated using existing literature. Also, the off-centre motion of a sphere in a microchannel is investigated, and theoretical predictions imply that the eccentricity of particle motion in a microchannel enhances both the translational and rotational velocity. Also, the planar motion of two spheres in a microchannel is studied using the current model. It is observed that, in the bulk fluid, particles with smaller size and larger zeta potential travel faster and can overtake larger particles or particles with lower zeta potential. However, the near wall motion of two spheres shows that the effect of zeta potential is overcome by an increase in electrical potential surrounding the particles, whereas the effect of particle size still remains dominant.

CHAPTER 6

CONCLUSION AND FUTURE DIRECTIONS

6.1 Conclusions and important contributions

1. Deterministic modeling of particle deposition from pressure driven flow in a parallel plate microchannel

This study deals with the deterministic modeling of particle deposition from pressure driven flow in a parallel plate microchannel. In the literature, effect of surface blocking on particle deposition in impinging jet flow cells has been investigated through an analytic Blocking function model that is valid for low surface coverages. Hence, this work is devoted to understanding the effect of surface blocking on particle deposition in parallel plate channels that possess enormous applications in microfluidics. The mass transport equations that incorporate hydrodynamic flow, colloidal and external forces are solved numerically, employing a variable transformation and Crank-Nicolson finite difference scheme. The analytic Blocking function based on RSA is derived for calculation of surface coverage. A parallel plate flow chamber is designed and an experimental test rig was developed to conduct videomicroscopic experiments for the quantification of particle deposition. The theoretical predictions incorporating the Blocking function model are compared with experimental results. The steady state theoretical results (Sherwood number that represents the dimensionless surface flux) are in reasonable agreement with the experimental data. However, it is found that the Blocking function is unable to model particle deposition for higher surface coverages.

CHAPTER 6**2. Brownian dynamic simulation and experimental study of particle deposition from pressure driven and electrokinetic microchannel flows**

Particle interactions play an important role in the transport and deposition in the case of flow of dense suspensions in microchannels. This problem becomes more interesting in the case of electrokinetic flows, as it has direct implications for Lab-on-a-Chip microfluidics. Existing studies in the literature focus on either pressure driven flow in impinging jet cells or are based on methods yielding simple analytical expressions that are valid for low surface concentrations of particles. Hence for moderate to high surface concentrations, a more comprehensive approach has to be followed. Motivated by this scenario, the irreversible adsorption of colloidal particles from pressure driven and electrokinetic flows in a parallel-plate microchannel has been investigated in this work. The Brownian dynamics simulation technique based on the stochastic Langevin equation is employed for computation of particle surface coverage. Deposition experiments using the parallel-plate flow technique were carried out to compare the simulation results, and a good agreement was found for the range of Reynolds numbers and electric field strengths studied. Further, the electrolyte concentration was found to influence the surface coverage significantly at lower Reynolds numbers; however such effect is reduced at higher Reynolds numbers due to the increased particle velocity and scattering of the moving particles in the vicinity of the deposited particles. In addition, as the particle size is reduced, the particle deposition increases due to increasing contributions of the colloidal interaction forces. Again, the effect of particle size starts decreasing at high Reynolds numbers. Particle deposition from pressure driven and electrokinetic flows are compared

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based on the flow Reynolds number, and it is found that higher surface coverage resulted in the latter. This is attributed to the opposing effect of electrophoresis and electroosmosis, when the particles and the channel wall bear the same charge polarity.

3. Electrokinetic transport of two spheres in a microchannel

This motivation for this study stems from the importance of boundary effects on particle transport in microfluidic devices. Interparticle interactions can play a significant role in particle transport and deposition, especially if the particles and channels are of comparable size. Through an analytical model developed in the present study, the electrokinetic transport of two spheres in a parallel plate microchannel is investigated. The solutions of Laplace equation governing the electrical potential and Stokes equation for the flow field are formulated analytically. This is performed by an analytical inversion of the Fourier transform of wall disturbances (expressed by Fourier integrals) to satisfy the boundary conditions on the surface of the spheres, where the disturbance due to the spheres are represented by spherical harmonic functions. The analytical results for the case of axisymmetric motion of a single sphere in a parallel plate microchannel are validated using the existing literature. Also, the off-centre motion of a sphere in a microchannel is investigated, and it is found that the eccentricity of particle motion in a microchannel enhances both the translational and rotational velocity. Furthermore, the planar motion of two spheres in a microchannel is studied using the present model. The theoretical results imply that, in the bulk fluid, particles with smaller size and larger zeta potential travel faster and can overtake larger particles or particles with lower zeta potential. However, the near wall motion of two spheres shows that the effect of zeta

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potential is overcome by an increase in electrical potential surrounding the particles, whereas the effect of particle size still remains dominant.

6.2 Future research directions

In this section, scope for future research and possible research directions are outlined towards a better understanding of particle transport and deposition in microchannels.

1. This dissertation aims to study particle deposition within the framework of DLVO theory, in which it is assumed that the interacting bodies are perfectly smooth. In real systems, however irregularities exist. Hence, in a microchannel with significant surface asperities, the hydrodynamic and colloidal interactions would be significantly altered. Hence, a fundamental understanding of particle transport in such situations is also important to the design and development of microfluidic devices.

2. The adsorption of particles can change the surface properties of the channel wall, including surface charge and surface potential. This would significantly affect the electrical interaction energy and the EDL expressions based on DLVO theory can no longer be used for computation. Hence, it would be worthwhile to look into modeling particle transport and deposition incorporating these effects. A mathematical model employing Gaussian distribution of surface potential is suggested for modeling the stochastic effects due to variation in surface potential.

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3. The analytical work presented in this thesis focus on the transport of spherical model particles in parallel plate microchannels. However, this may not be the case always, especially when considering some bioparticles such as DNA. Some bioparticles can be of arbitrary shape, for example disc or rod shaped. These geometries can be effectively modeled by considering prolate and oblate spheroidal geometries, respectively. Since the governing equations of electrical potential and flow field are linear, one can possibly employ the superposition of the disturbances due to the particles (represented by spheroidal harmonic functions), and wall disturbances represented by Fourier integrals. This indeed is challenging from the mathematical point of view. An alternative for the above problem is to employ boundary integral equation technique which is quite popular in dealing with complex surface shapes.

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APPENDIX 1

Hydrodynamic mobility tensor for the relative motion of two spheres in the presence of a plane wall

The problem of relative motion of two spheres in three dimensional space has been studied by several authors (Batchelor, 1976; Adler, 1971; Jeffery and Onishi, 1984). The Hydrodynamic mobility tensor, $\mathbf{M}_{ij}$, for the interaction of two spheres in the vicinity of a plane wall (presented in equation (4.16)) can be expressed as (Beenacker et al., 1984),

$$\mathbf{M}_{ij} = \frac{1}{6\pi\mu a_i} \left\{ \begin{aligned} & \left[\mathbf{I}\delta_{ij} + \left[\frac{3}{4}a_i r^{-1}(\mathbf{I} + \mathbf{e}_{ij}\mathbf{e}_{ij}) - \frac{3}{4}a_i(a_i^2 + a_j^2)r^{-3} \left(\mathbf{e}_{ij}\mathbf{e}_{ij} - \frac{1}{3}\mathbf{I} \right) \right] (1 - \delta_{ij}) \right] \\ & - \frac{3}{4}a_i r_s^{-1} \left[\mathbf{I} + \mathbf{e}_{ij}\mathbf{e}_{ij} - 2l_i r_s^{-1} \mathbf{e}_{ij}\mathbf{n} + 2l_j r_s^{-1} \mathbf{n}\mathbf{e}_{ij} + 2l_i l_j r_s^{-2} \right] \\ & \left[(\mathbf{I} - 2\mathbf{n}\mathbf{n} - 3\mathbf{e}_{ij}\mathbf{e}_{ij}) \right] \\ & + \frac{3}{4}a_i(a_i^2 + a_j^2)r_s^{-3} \left(\mathbf{e}_{ij}\mathbf{e}_{ij} - \frac{1}{3}\mathbf{I} \right) - \frac{3}{2}a_i(a_i^2 - a_j^2)r_s^{-4} (l_i \mathbf{e}_{ij}\mathbf{n} + l_j \mathbf{n}\mathbf{e}_{ij}) \\ & + \frac{3}{2}a_i r_s^{-5} (a_i^2 l_j + a_j^2 l_i) (l_i + l_j) (\mathbf{I} - 2\mathbf{n}\mathbf{n} - 5\mathbf{e}_{ij}\mathbf{e}_{ij}) \end{aligned} \right\} \quad (\text{A1.1})$$

where

$$\begin{aligned} \mathbf{e}_{ij} &= \frac{\mathbf{S} \cdot \mathbf{r}_j - \mathbf{r}_i}{r_s} & \mathbf{e}_{ij} &= \frac{\mathbf{r}_j - \mathbf{S} \cdot \mathbf{r}_i}{r_s} & \mathbf{e}_{ij} &= \frac{\mathbf{r}_j - \mathbf{r}_i}{r} & r &= |\mathbf{r}_j - \mathbf{r}_i| \\ l_i &= \mathbf{n} \cdot \mathbf{r}_i & l_j &= \mathbf{n} \cdot \mathbf{r}_j & \mathbf{S} &= \mathbf{I} - 2\mathbf{n}\mathbf{n} & r_s &= |\mathbf{S} \cdot \mathbf{r}_j - \mathbf{r}_i| \end{aligned} \quad (\text{A1.2})$$

In the above equations, $\mathbf{I}$ represents the second order unit tensor and $\mathbf{n}$ represents the unit vector normal to the surface, $\mathbf{r}_i$ and $\mathbf{r}_j$ represent the position vectors of i^{th} and j^{th} spheres and a_i and a_j are the radii of i^{th} and j^{th} spheres. For $i = j$ the expression given above reduce to the diffusion tensor for a single particle near to a plane wall, and, for $l_i, l_j \rightarrow \infty$,

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to the Rotne-Prager tensor for two spheres in an unbounded medium which is expressed as (Elimelech et al., 1995)

$$D_{ij} = \frac{1}{6\pi\mu a} \left[I\delta_{ij} + (1-\delta_{ij}) \frac{3}{4} \frac{a}{r} \left(I + \frac{\mathbf{r}_{ij}\mathbf{r}_{ij}}{r^2} \right) - (1-\delta_{ij}) \frac{1}{2} \left(\frac{a}{r} \right)^3 \left(3 \frac{\mathbf{r}_{ij}\mathbf{r}_{ij}}{r^2} - I \right) \right] \quad (\text{A1.3})$$

APPENDIX 2

Analytical expressions for electrical potential distribution and the functions $H_{11}(x, y, z)$ to $H_{33}(x, y, z)$ presented in Chapter 5

Expression for the electrical potential distribution

The electrical potential in the fluid, $\phi = \phi_{w1c} + \phi_{w2c} + \phi_{w1nc} + \phi_{w2nc} + \phi_s$, where

$$\phi_{w1c} = \sum_{n=0}^{\infty} \sum_{k=0}^n \sum_{s=0}^{[n/2]} \left\{ \begin{aligned} & -b(n+1)R_{1kn} \int_0^{\infty} \frac{2\pi \exp[\kappa(z+b)] J_k(\kappa\rho)}{[\exp(-2\kappa b) - \exp(2\kappa c)]} V_{1nsk}^* \cos(k\varphi_1) d\kappa \\ & -b(n+1)S_{1kn} \int_0^{\infty} \frac{2\pi \exp[\kappa(z+b)] J_k(\kappa\rho)}{[\exp(-2\kappa b) - \exp(2\kappa c)]} V_{1nsk}^* \sin(k\varphi_1) d\kappa \\ & +R_{1kn} \int_0^{\infty} \frac{2\pi \exp[\kappa(z+b)] J_k(\kappa\rho)}{[\exp(-2\kappa b) - \exp(2\kappa c)]} V_{2nsk}^* \cos(k\varphi_1) d\kappa \\ & +S_{1kn} \int_0^{\infty} \frac{2\pi \exp[\kappa(z+b)] J_k(\kappa\rho)}{[\exp(-2\kappa b) - \exp(2\kappa c)]} V_{2nsk}^* \sin(k\varphi_1) d\kappa \\ & +c(n+1)R_{1kn} \int_0^{\infty} \frac{2\pi \exp[\kappa(z+c)] J_k(\kappa\rho)}{[\exp(-2\kappa b) - \exp(2\kappa c)]} V_{5nsk}^* \cos(k\varphi_1) d\kappa \\ & +c(n+1)S_{1kn} \int_0^{\infty} \frac{2\pi \exp[\kappa(z+c)] J_k(\kappa\rho)}{[\exp(-2\kappa b) - \exp(2\kappa c)]} V_{5nsk}^* \sin(k\varphi_1) d\kappa \\ & -R_{1kn} \int_0^{\infty} \frac{2\pi \exp[\kappa(z+c)] J_k(\kappa\rho)}{[\exp(-2\kappa b) - \exp(2\kappa c)]} V_{6nsk}^* \cos(k\varphi_1) d\kappa \\ & -S_{1kn} \int_0^{\infty} \frac{2\pi \exp[\kappa(z+c)] J_k(\kappa\rho)}{[\exp(-2\kappa b) - \exp(2\kappa c)]} V_{6nsk}^* \sin(k\varphi_1) d\kappa \end{aligned} \right\} \quad (A2.1)$$

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$$\phi_{w2c} = \sum_{n=0}^{\infty} \sum_{k=0}^n \left\{ \begin{aligned} & -b(n+1)R_{1kn} \int_0^{\infty} \frac{2\pi \exp[-\kappa(z-b-2c)] J_k(\kappa\rho)}{[\exp(-2\kappa b) - \exp(2\kappa c)]} V_{1nsk}^* \cos(k\varphi_1) d\kappa \\ & -b(n+1)S_{1kn} \int_0^{\infty} \frac{2\pi \exp[-\kappa(z-b-2c)] J_k(\kappa\rho)}{[\exp(-2\kappa b) - \exp(2\kappa c)]} V_{1nsk}^* \sin(k\varphi_1) d\kappa \\ & +R_{1kn} \int_0^{\infty} \frac{2\pi \exp[-\kappa(z-b-2c)] J_k(\kappa\rho)}{[\exp(-2\kappa b) - \exp(2\kappa c)]} V_{2nsk}^* \cos(k\varphi_1) d\kappa \\ & +S_{1kn} \int_0^{\infty} \frac{2\pi \exp[-\kappa(z-b-2c)] J_k(\kappa\rho)}{[\exp(-2\kappa b) - \exp(2\kappa c)]} V_{2nsk}^* \sin(k\varphi_1) d\kappa \\ & +c(n+1)R_{1kn} \int_0^{\infty} \frac{2\pi \exp[-\kappa(z-2b-c)] J_k(\kappa\rho)}{[\exp(-2\kappa b) - \exp(2\kappa c)]} V_{5nsk}^* \cos(k\varphi_1) d\kappa \\ & +c(n+1)S_{1kn} \int_0^{\infty} \frac{2\pi \exp[-\kappa(z-2b-c)] J_k(\kappa\rho)}{[\exp(-2\kappa b) - \exp(2\kappa c)]} V_{5nsk}^* \sin(k\varphi_1) d\kappa \\ & -R_{1kn} \int_0^{\infty} \frac{2\pi \exp[-\kappa(z-2b-c)] J_k(\kappa\rho)}{[\exp(-2\kappa b) - \exp(2\kappa c)]} V_{6nsk}^* \cos(k\varphi_1) d\kappa \\ & -S_{1kn} \int_0^{\infty} \frac{2\pi \exp[-\kappa(z-2b-c)] J_k(\kappa\rho)}{[\exp(-2\kappa b) - \exp(2\kappa c)]} V_{6nsk}^* \sin(k\varphi_1) d\kappa \end{aligned} \right\} \quad (A2.2)$$

where, $(-1)^{2k} \int_0^{\infty} F_1^*(\rho) d\rho = V_{1nsk}^*$

$$V_{1nsk}^* = \sum_{s=0}^{[n/2]} \left\{ \begin{aligned} & \frac{(-1)^{s+1} (2n-2s)!}{s!(n-s)!(n-2s)!} \frac{\Gamma(n-2s+1)}{\Gamma(n-2s-k+1)} b^{n-2s-k} \\ & \left[\frac{b^{k-n+s-1/2} \kappa^{n-s+1/2}}{2^{2n-s+1/2} \Gamma(n-s+3/2)} \right] K_{k-(n-s+1/2)}(\kappa b) \end{aligned} \right\} \quad (A2.3)$$

$$V_{1nsk}^* = \sum_{s=0}^{[n/2]} \left\{ \begin{aligned} & \frac{(-1)^{s+1} (2n-2s)!}{s!(n-s)!(n-2s)!} \frac{\Gamma(n-2s+1)}{\Gamma(n-2s-k+1)} b^{-(s+1/2)} \\ & \left[\frac{\kappa^{n-s+1/2}}{2^{2n-s+1/2} \Gamma(n-s+3/2)} \right] K_{k-(n-s+1/2)}(\kappa b) \end{aligned} \right\} \quad (A2.4)$$

Similarly,

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$$V_{2nsk}^* = \left\{ \begin{aligned} & b(n+1) \sum_{s=0}^{[n/2]} \left\{ \frac{(-1)^{s+1} (2n-2s)!}{s!(n-s)!(n-2s)!} \frac{\Gamma(n-2s+1)}{\Gamma(n-2s-k+1)} b^{-s} \right. \\ & \quad \left. \left[\frac{\kappa^{n-s}}{2^{2n-s} \Gamma(n-s+1)} \right] K_{k-n+s}(\kappa b) \right\} \\ & - (n-k+1) \sum_{s=0}^{[(n+1)/2]} \left\{ \frac{(-1)^{s+1} [2(n+1)-2s]!}{s!(n+1-s)!(n+1-2s)!} \frac{\Gamma(n-2s+2)}{\Gamma(n-2s-k+2)} b^{1-s} \right. \\ & \quad \left. \left[\frac{\kappa^{n-s}}{2^{2n-s} \Gamma(n-s+1)} \right] K_{k-n+s}(\kappa b) \right\} \end{aligned} \right\} \quad (A2.5)$$

$$V_{5nsk}^* = \sum_{s=0}^{[n/2]} \left\{ \frac{(-1)^{s+1} (2n-2s)!}{s!(n-s)!(n-2s)!} \frac{\Gamma(n-2s+1)}{\Gamma(n-2s-k+1)} c^{-(s+1/2)} \right. \\ \left. \left[\frac{\kappa^{n-s+1/2}}{2^{2n-s+1/2} \Gamma(n-s+3/2)} \right] K_{k-(n-s+1/2)}(\kappa c) \right\} \quad (A2.6)$$

$$V_{6nsk}^* = \left\{ \begin{aligned} & c(n+1) \sum_{s=0}^{[n/2]} \left\{ \frac{(-1)^{s+1} (2n-2s)!}{s!(n-s)!(n-2s)!} \frac{\Gamma(n-2s+1)}{\Gamma(n-2s-k+1)} c^{-s} \right. \\ & \quad \left. \left[\frac{\kappa^{n-s}}{2^{2n-s} \Gamma(n-s+1)} \right] K_{k-n+s}(\kappa c) \right\} \\ & - (n-k+1) \sum_{s=0}^{[(n+1)/2]} \left\{ \frac{(-1)^{s+1} [2(n+1)-2s]!}{s!(n+1-s)!(n+1-2s)!} \frac{\Gamma(n-2s+2)}{\Gamma(n-2s-k+2)} c^{1-s} \right. \\ & \quad \left. \left[\frac{\kappa^{n-s}}{2^{2n-s} \Gamma(n-s+1)} \right] K_{k-n+s}(\kappa c) \right\} \end{aligned} \right\} \quad (A2.7)$$

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$$\phi_{w1nc} = \sum_{n=0}^{\infty} \sum_{k=0}^n \left\{ \begin{aligned} & -(n+1)R_{1kn} \int_0^{\infty} \frac{2\pi \exp[\kappa(z+b)] J_k(\kappa\rho)}{[\exp(-2\kappa b) - \exp(2\kappa c)]} H_{nn3} \cos(k\varphi_1) d\kappa \\ & -(n+1)S_{1kn} \int_0^{\infty} \frac{2\pi \exp[\kappa(z+b)] J_k(\kappa\rho)}{[\exp(-2\kappa b) - \exp(2\kappa c)]} H_{nn3} \sin(k\varphi_1) d\kappa \\ & + R_{1kn} \int_0^{\infty} \frac{2\pi \exp[\kappa(z+b)] J_k(\kappa\rho)}{[\exp(-2\kappa b) - \exp(2\kappa c)]} H_{nn4} \cos(k\varphi_1) d\kappa \\ & + S_{1kn} \int_0^{\infty} \frac{2\pi \exp[\kappa(z+b)] J_k(\kappa\rho)}{[\exp(-2\kappa b) - \exp(2\kappa c)]} H_{nn4} \sin(k\varphi_1) d\kappa \\ & + (n+1)R_{1kn} \int_0^{\infty} \frac{2\pi \exp[\kappa(z+c)] J_k(\kappa\rho)}{[\exp(-2\kappa b) - \exp(2\kappa c)]} H_{nn7} \cos(k\varphi_1) d\kappa \\ & + (n+1)S_{1kn} \int_0^{\infty} \frac{2\pi \exp[\kappa(z+c)] J_k(\kappa\rho)}{[\exp(-2\kappa b) - \exp(2\kappa c)]} H_{nn7} \sin(k\varphi_1) d\kappa \\ & - R_{1kn} \int_0^{\infty} \frac{2\pi \exp[\kappa(z+c)] J_k(\kappa\rho)}{[\exp(-2\kappa b) - \exp(2\kappa c)]} H_{nn8} \cos(k\varphi_1) d\kappa \\ & - S_{1kn} \int_0^{\infty} \frac{2\pi \exp[\kappa(z+c)] J_k(\kappa\rho)}{[\exp(-2\kappa b) - \exp(2\kappa c)]} H_{nn8} \sin(k\varphi_1) d\kappa \end{aligned} \right\} \quad (A2.8)$$

where

$$H_{nni}(\kappa) = \int_0^{\infty} f_{ni}(\rho) J_n(\kappa\rho) \rho d\rho \quad (A2.9)$$

and

$$f(\rho, \varphi_1) = \sum_{n=-\infty}^{\infty} f_{ni}(\rho) \exp(ik\varphi_1) \quad (A2.10)$$

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$$\phi_{w2nc} = \sum_{n=0}^{\infty} \sum_{k=0}^n \left\{ \begin{aligned}
& -(n+1)R_{1kn} \int_0^{\infty} \frac{2\pi \exp[-\kappa(z-b-2c)] J_k(\kappa\rho)}{[\exp(-2\kappa b) - \exp(2\kappa c)]} H_{nn3} \cos(k\varphi_1) d\kappa \\
& -(n+1)S_{1kn} \int_0^{\infty} \frac{2\pi \exp[-\kappa(z-b-2c)] J_k(\kappa\rho)}{[\exp(-2\kappa b) - \exp(2\kappa c)]} H_{nn3} \sin(k\varphi_1) d\kappa \\
& + R_{1kn} \int_0^{\infty} \frac{2\pi \exp[-\kappa(z-b-2c)] J_k(\kappa\rho)}{[\exp(-2\kappa b) - \exp(2\kappa c)]} H_{nn4} \cos(k\varphi_1) d\kappa \\
& + S_{1kn} \int_0^{\infty} \frac{2\pi \exp[-\kappa(z-b-2c)] J_k(\kappa\rho)}{[\exp(-2\kappa b) - \exp(2\kappa c)]} H_{nn4} \sin(k\varphi_1) d\kappa \\
& + (n+1)R_{1kn} \int_0^{\infty} \frac{2\pi \exp[-\kappa(z-2b-c)] J_k(\kappa\rho)}{[\exp(-2\kappa b) - \exp(2\kappa c)]} H_{nn7} \cos(k\varphi_1) d\kappa \\
& + (n+1)S_{1kn} \int_0^{\infty} \frac{2\pi \exp[-\kappa(z-2b-c)] J_k(\kappa\rho)}{[\exp(-2\kappa b) - \exp(2\kappa c)]} H_{nn7} \sin(k\varphi_1) d\kappa \\
& - R_{1kn} \int_0^{\infty} \frac{2\pi \exp[-\kappa(z-2b-c)] J_k(\kappa\rho)}{[\exp(-2\kappa b) - \exp(2\kappa c)]} H_{nn8} \cos(k\varphi_1) d\kappa \\
& - S_{1kn} \int_0^{\infty} \frac{2\pi \exp[-\kappa(z-2b-c)] J_k(\kappa\rho)}{[\exp(-2\kappa b) - \exp(2\kappa c)]} H_{nn8} \sin(k\varphi_1) d\kappa
\end{aligned} \right\} \quad (A2.11)$$

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Analytical Expressions for the functions $H_{11}(x, y, z)$ to $H_{33}(x, y, z)$

$$H_{11}(x, y, z) = \left\{ \begin{aligned} & \left[\frac{-(n+1)}{r_1^{(n+2)}} P_n^k(q_1) (C_{1kn} \cos k\varphi_1 + D_{1kn} \sin k\varphi_1) \right. \\ & \left. + \frac{(n+1)}{2\mu(2n-1)} \frac{P_n^k(q_1)}{r_1^n} (E_{1kn} \cos k\varphi_1 + F_{1kn} \sin k\varphi_1) \right] \\ & \sin \theta_1 \cos \varphi_1 \\ & + \left[-\frac{k}{r_1^{(n+1)} \sin \theta_1} P_n^k(q_1) (A_{1kn} \sin k\varphi_1 - B_{1kn} \cos k\varphi_1) \right. \\ & - \frac{\sin \theta_1}{r_1^{(n+2)}} \frac{dP_n^k(q_1)}{dq_1} (C_{1kn} \cos k\varphi_1 + D_{1kn} \sin k\varphi_1) \\ & \left. + \frac{(n-2) \sin \theta_1}{2n\mu(2n-1)r_1^n} \frac{dP_n^k(q_1)}{dq_1} (E_{1kn} \cos k\varphi_1 + F_{1kn} \sin k\varphi_1) \right] \\ & \cos \theta_1 \cos \varphi_1 \\ & - \left[\frac{\sin \theta_1}{r_1^{(n+1)}} \frac{dP_n^k(q_1)}{dq_1} (A_{1kn} \cos k\varphi_1 + B_{1kn} \sin k\varphi_1) \right. \\ & - \frac{k}{r_1^{(n+2)} \sin \theta_1} P_n^k(q_1) (C_{1kn} \sin k\varphi_1 - D_{1kn} \cos k\varphi_1) \\ & \left. + \frac{(n-2)kP_n^k(q_1)}{2n\mu(2n-1)r_1^n \sin \theta_1} (E_{1kn} \sin k\varphi_1 + F_{1kn} \cos k\varphi_1) \right] \\ & \sin \varphi_1 \end{aligned} \right\} \quad (A2.12)$$

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$$H_{12}(x, y, z) = \left\{ \begin{aligned} & \left(\frac{-(n+1)}{r_2^{(n+2)}} P_n^k(q_2) (C_{2kn} \cos k\varphi_2 + D_{2kn} \sin k\varphi_2) \right. \\ & \left. + \frac{(n+1)}{2\mu(2n-1)} \frac{P_n^k(q_2)}{r_2^n} (E_{2kn} \cos k\varphi_2 + F_{2kn} \sin k\varphi_2) \right) \\ & (f_{121} \sin \theta_1 \cos \varphi_1 + f_{221} \cos \theta_1 \cos \varphi_1 - f_{321} \sin \varphi_1) \\ & + \left(-\frac{k}{r_2^{(n+1)} \sin \theta_1} P_n^k(q_2) (A_{2kn} \sin k\varphi_2 - B_{2kn} \cos k\varphi_2) \right. \\ & - \frac{\sin \theta_2}{r_2^{(n+2)}} \frac{dP_n^k(q_2)}{dq_2} (C_{2kn} \cos k\varphi_2 + D_{2kn} \sin k\varphi_2) \\ & \left. + \frac{(n-2) \sin \theta_2}{2n\mu(2n-1)r_2^n} \frac{dP_n^k(q_2)}{dq_2} (E_{2kn} \cos k\varphi_2 + F_{2kn} \sin k\varphi_2) \right) \\ & (f_{421} \sin \theta_1 \cos \varphi_1 + f_{521} \cos \theta_1 \cos \varphi_1 - f_{621} \sin \varphi_1) \end{aligned} \right\} \quad (A2.13)$$

$$H_{13}(x, y, z) = \left\{ \begin{aligned} & -\frac{\sin \theta_2}{r_2^{(n+1)}} \frac{dP_n^k(q_2)}{dq_2} (A_{2kn} \cos k\varphi_2 + B_{2kn} \sin k\varphi_2) \\ & -\frac{k}{r_2^{(n+2)} \sin \theta_2} P_n^k(q_2) (C_{2kn} \sin k\varphi_2 - D_{2kn} \cos k\varphi_2) \\ & + \frac{(n-2)kP_n^k(q_2)}{2n\mu(2n-1)r_2^n \sin \theta_2} (E_{2kn} \sin k\varphi_2 - F_{2kn} \cos k\varphi_2) \\ & (f_{721} \sin \theta_1 \cos \varphi_1 + f_{821} \cos \theta_1 \cos \varphi_1 - f_{921} \sin \varphi_1) \end{aligned} \right\} \quad (A2.14)$$

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$$H_{21}(x, y, z) = \left\{ \begin{aligned} & \left[\begin{aligned} & \frac{-(n+1)}{r_1^{(n+2)}} P_n^k(q_1) (C_{1kn} \cos k\varphi_1 + D_{1kn} \sin k\varphi_1) \\ & + \frac{(n+1)}{2\mu(2n-1)} \frac{P_n^k(q_1)}{r_1^n} (E_{1kn} \cos k\varphi_1 + F_{1kn} \sin k\varphi_1) \end{aligned} \right] \\ & \sin \theta_1 \sin \varphi_1 \\ & \left[\begin{aligned} & -\frac{k}{r_1^{(n+1)} \sin \theta_1} P_n^k(q_1) (A_{1kn} \sin k\varphi_1 - B_{1kn} \cos k\varphi_1) \\ & + \frac{\sin \theta_1}{r_1^{(n+2)}} \frac{dP_n^k(q_1)}{dq_1} (C_{1kn} \cos k\varphi_1 + D_{1kn} \sin k\varphi_1) \\ & + \frac{(n-2) \sin \theta_1}{2n\mu(2n-1)r_1^n} \frac{dP_n^k(q_1)}{dq_1} (E_{1kn} \cos k\varphi_1 + F_{1kn} \sin k\varphi_1) \end{aligned} \right] \\ & \cos \theta_1 \sin \varphi_1 \\ & \left[\begin{aligned} & \frac{\sin \theta_1}{r_1^{(n+1)}} \frac{dP_n^k(q_1)}{dq_1} (A_{1kn} \cos k\varphi_1 + B_{1kn} \sin k\varphi_1) \\ & + \frac{k}{r_1^{(n+2)} \sin \theta_1} P_n^k(q_1) (C_{1kn} \sin k\varphi_1 - D_{1kn} \cos k\varphi_1) \\ & + \frac{(n-2)kP_n^k(q_1)}{2n\mu(2n-1)r_1^n \sin \theta_1} (E_{1kn} \sin k\varphi_1 + F_{1kn} \cos k\varphi_1) \end{aligned} \right] \\ & \cos \varphi_1 \end{aligned} \right\} \quad (A2.15)$$

$$H_{22}(x, y, z) = \left\{ \begin{aligned} & \left[\begin{aligned} & \frac{-(n+1)}{r_2^{(n+2)}} P_n^k(q_2) (C_{2kn} \cos k\varphi_2 + D_{2kn} \sin k\varphi_2) \\ & + \frac{(n+1)}{2\mu(2n-1)} \frac{P_n^k(q_2)}{r_2^n} (E_{2kn} \cos k\varphi_2 + F_{2kn} \sin k\varphi_2) \end{aligned} \right] \\ & (f_{121} \sin \theta_1 \sin \varphi_1 + f_{221} \cos \theta_1 \sin \varphi_1 + f_{321} \cos \varphi_1) \\ & \left[\begin{aligned} & -\frac{k}{r_2^{(n+1)} \sin \theta_1} P_n^k(q_2) (A_{2kn} \sin k\varphi_2 - B_{2kn} \cos k\varphi_2) \\ & + \frac{\sin \theta_2}{r_2^{(n+2)}} \frac{dP_n^k(q_2)}{dq_2} (C_{2kn} \cos k\varphi_2 + D_{2kn} \sin k\varphi_2) \\ & + \frac{(n-2) \sin \theta_2}{2n\mu(2n-1)r_2^n} \frac{dP_n^k(q_2)}{dq_2} (E_{2kn} \cos k\varphi_2 + F_{2kn} \sin k\varphi_2) \end{aligned} \right] \\ & (f_{421} \sin \theta_1 \sin \varphi_1 + f_{521} \cos \theta_1 \sin \varphi_1 + f_{621} \cos \varphi_1) \end{aligned} \right\} \quad (A2.16)$$

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$$H_{23}(x, y, z) = \left\{ \begin{aligned} & \frac{\sin \theta_2}{r_2^{(n+1)}} \frac{dP_n^k(q_2)}{dq_2} (A_{2kn} \cos k\varphi_2 + B_{2kn} \sin k\varphi_2) \\ & - \frac{k}{r_2^{(n+2)} \sin \theta_2} P_n^k(q_2) (C_{2kn} \sin k\varphi_2 - D_{2kn} \cos k\varphi_2) \\ & + \frac{(n-2)kP_n^k(q_2)}{2n\mu(2n-1)r_2^n \sin \theta_2} (E_{2kn} \sin k\varphi_2 - F_{2kn} \cos k\varphi_2) \\ & (f_{721} \sin \theta_1 \sin \varphi_1 + f_{821} \cos \theta_1 \sin \varphi_1 + f_{921} \cos \varphi_1) \end{aligned} \right\} \quad (A2.17)$$

$$H_{31}(x, y, z) = \left\{ \begin{aligned} & \left(\frac{-(n+1)}{r_1^{(n+2)}} P_n^k(q_1) (C_{1kn} \cos k\varphi_1 + D_{1kn} \sin k\varphi_1) \right. \\ & \left. + \frac{(n+1)}{2\mu(2n-1)} \frac{P_n^k(q_1)}{r_1^n} (E_{1kn} \cos k\varphi_1 + F_{1kn} \sin k\varphi_1) \right) \cos \theta_1 \\ & - \left(\frac{k}{r_1^{(n+1)} \sin \theta_1} P_n^k(q_1) (A_{1kn} \sin k\varphi_1 - B_{1kn} \cos k\varphi_1) \right. \\ & - \frac{\sin \theta_1}{r_1^{(n+2)}} \frac{dP_n^k(q_1)}{dq_1} (C_{1kn} \cos k\varphi_1 + D_{1kn} \sin k\varphi_1) \\ & \left. + \frac{(n-2) \sin \theta_1}{2n\mu(2n-1)r_1^n} \frac{dP_n^k(q_1)}{dq_1} (E_{1kn} \cos k\varphi_1 + F_{1kn} \sin k\varphi_1) \right) \sin \theta_1 \end{aligned} \right\} \quad (A2.18)$$

$$H_{32}(x, y, z) = \left\{ \begin{aligned} & \left(\frac{-(n+1)}{r_2^{(n+2)}} P_n^k(q_2) (C_{2kn} \cos k\varphi_2 + D_{2kn} \sin k\varphi_2) \right. \\ & \left. + \frac{(n+1)}{2\mu(2n-1)} \frac{P_n^k(q_2)}{r_2^n} (E_{2kn} \cos k\varphi_2 + F_{2kn} \sin k\varphi_2) \right) \\ & (f_{121} \cos \theta_1 - f_{221} \sin \theta_1) \\ & + \left(-\frac{k}{r_2^{(n+1)} \sin \theta_1} P_n^k(q_2) (A_{2kn} \sin k\varphi_2 - B_{2kn} \cos k\varphi_2) \right. \\ & - \frac{\sin \theta_2}{r_2^{(n+2)}} \frac{dP_n^k(q_2)}{dq_2} (C_{2kn} \cos k\varphi_2 + D_{2kn} \sin k\varphi_2) \\ & \left. + \frac{(n-2) \sin \theta_2}{2n\mu(2n-1)r_2^n} \frac{dP_n^k(q_2)}{dq_2} (E_{2kn} \cos k\varphi_2 + F_{2kn} \sin k\varphi_2) \right) \\ & (f_{421} \cos \theta_1 - f_{521} \sin \theta_1) \end{aligned} \right\} \quad (A2.19)$$

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$$H_{33}(x, y, z) = \left\{ \begin{aligned} & \frac{\sin \theta_2}{r_2^{(n+1)}} \frac{dP_n^k(q_2)}{dq_2} (A_{2kn} \cos k\varphi_2 + B_{2kn} \sin k\varphi_2) \\ & - \frac{k}{r_2^{(n+2)} \sin \theta_2} P_n^k(q_2) (C_{2kn} \sin k\varphi_2 - D_{2kn} \cos k\varphi_2) \\ & + \frac{(n-2)kP_n^k(q_2)}{2n\mu(2n-1)r_2^n \sin \theta_2} (E_{2kn} \sin k\varphi_2 + F_{2kn} \cos k\varphi_2) \\ & (f_{721} \cos \theta_1 - f_{821} \sin \theta_1) \end{aligned} \right\} \quad (\text{A2.20})$$