NORTHWESTERN UNIVERSITY

Electroosmotic Flow and Dispersion in Microfluidic Separation Systems

A DISSERTATION

SUBMITTED TO THE GRADUATE SCHOOL IN PARTIAL FULFILLMENT OF THE REQUIREMENTS

for the degree

DOCTOR OF PHILOSOPHY

Field of Mechanical Engineering

By

Subhra Datta

EVANSTON, ILLINOIS

June 2007

 \bigodot Copyright by Subhra Datta 2007

All Rights Reserved

ABSTRACT

Electroosmotic Flow and Dispersion in Microfluidic Separation Systems

Subhra Datta

Motivated by applications to microfluidic separation systems like Capillary Electrophoresis (CE) and Capillary Electrochromatography (CEC), the research described in this dissertation analyzes through numerical and asymptotic methods the effect of variation in the wall zeta potential (or surface charge) on the electroosmotic flow field in a microchannel and the effect of inhomogeneities in the flow field and wall interactions on the dispersion (spreading) of a solute undergoing separation in a microchannel.

The electroosmotic flow field is solved numerically in a rectangular microchannel with several representative zeta potential distributions on the wall. When the axial scale of variation of zeta potential is larger than the microchannel width, the numerical results show good agreement with an asymptotic analysis based on lubrication theory. In the opposite limit, when the axial scale of variation in zeta potential is smaller than the microchannel width, the numerical results indicate that a parallel plate approximation of the rectangular geometry serves as an adequate model.

The transport of a solute in a straight microchannel of arbitrary cross-section in presence of an adsorption-desorption process on the wall is studied. An asymptotic approach valid in the long time limit is developed that leads to the formulation of a one-dimensional partial differential equation for the cross-sectionally averaged solute concentration. Integration of this equation is much less expensive computationally compared to the numerical solution of the full three-dimensional problem. Further, the asymptotically reduced model allows us to calculate the three-dimensional concentration field in the microchannel algebraically, once the axial distribution of the cross-sectionally averaged concentration has been calculated. In the limit when adsorption and desorption are at least as fast as the cross-diffusion, useful analytical expressions applicable to dispersion calculations in CEC and a wide variety of chromatographic separations are obtained from this model. The asymptotic analysis is also extended to handle axial variations in the flow field and the cross-sectional shape. Several test problems are solved in a rectangular microchannel through asymptotic reduction as well as through complete numerical solution in three dimensions. The results from the threedimensional numerical solution are found to be in good agreement with the results from the asymptotically reduced model.

Acknowledgements

The work presented here could not have been performed without the help of many people. I would like to record here my gratitude to those who have helped me through my study and thesis work at Northwestern University.

I am deeply indebted to my thesis advisor Prof. Sandip Ghosal for his guidance and support during the course of this research. I am thankful to him for providing me an interesting dissertation topic to research on and for guiding my nascent interests in the field of microfluidics, electrokinetic phenomena, separation science and asymptotic analysis. His invaluable guidance has made my research experience at Northwestern University meaningful and intellectually stimulating. I am also grateful for his help with my postdoctoral applications and career planning. I am thankful to Prof. Neelesh A. Patankar and Prof. Seth H. Lichter for being part of my final examination committee and for writing letters of recommendation for my postdoctoral applications. I am thankful to Prof. Neelesh A. Patankar for his guidance in performing numerical computations and for providing me with a computer program to solve the flow and scalar fields in a rectangular channel. I am also thankful to Dr. Karim Shariff at the Nasa Ames Research Center for his guidance in performing numerical computations and for providing me a computer program for solving the scalar field in an axisymmetric cylinder. I am thankful to my parents and brother for their continuous encouragement during the course of my research. I also thank my officemates and friends for personal support and for maintaining a harmonious research environment.

List of Abbreviations

2-D	Two Dimensional
3-D	Three Dimensional
CE	Capillary Electrophoresis
CEC	Capillary Electrochromatography
EDL	Electrical Double Layer
EOF	Electroosmotic Flow
HETP	Height Equivalent of Theoretical Plates
HS	Helmholtz-Smoluchowski
LC	Liquid Chromatography
LEP	Low Electrostatic Potential
PDMS	Polydimethylsiloxane
TDMA	Tridiagonal Matrix Algorithm
TDL	Thin Debye Layer

Table of Contents

ABSTRACT	3	
Acknowledgements	5	
List of Abbreviations	6	
List of Tables	12	
List of Figures	13	
Chapter 1. Introduction	16	
1.1. Electroosmosis and Electrophoresis	16	
1.2. Electrokinetic Phenomena in Microfluidic Separation Systems	16	
1.3. Key Physical concepts	19	
1.4. Effect of Inhomogeneities in EOF and Wall Interactions on Separations	20	
1.5. Objectives 26		
Chapter 2. Electroosmotic Flow and Dispersion in Microfluidic Separation Systems:		
Fundamentals	29	
2.1. Gouy Chapman Model of the EDL	30	
2.2. The Debye-Hückel Approximation	31	
2.3. Solution for Flow in EDL under External Electric Field	33	
2.4. The Thin Debye Layer (TDL) Limit for EOF 34		

2.5. The Plug Flow Solution of EOF	35
2.6. Flows with Axial Variation	35
2.6.1. Exact Solutions	36
2.6.2. Solution in the Lubrication Limit	38
2.7. Consequences of Axial Variation of Zeta Potential in CE channels	38
2.8. Dispersion in Microfluidic Systems	39
2.9. Taylor-Aris Dispersion with Inert Walls	40
2.10. Taylor-Aris Dispersion with Active Walls	41
2.10.1. Dispersion with Irreversible Wall Loss	41
2.10.2. Dispersion with Reversible Adsorption-Desorption on Walls	42
2.11. Dispersion in Axially variable Flows With Wall Interactions	43
2.12. Summary	44

Chapte	er 3. Electroosmotic Flow in a Rectangular Channel under Axially Variable Zeta	
	Potential	45
3.1.	Background	45
3.1.1	. Governing Equations	45
3.1.2	Analytical results from Lubrication Theory	48
3.1.3	Analytical result for Stokes Flow between Parallel Plates	54
3.2.	Test Problems for Numerical Simulation of Electroosmotic Flow with Variable	
	Zeta Potential	56
3.3.	Numerical Methods	59
3.4.	Comparison of Numerical Simulations to Asymptotic Theory	61

Theory	61
3.4.2. Transition from Slow to Fast Variation in Wall Zeta Potential	76
3.5. Summary	82
Chapter 4. Dispersion in the Presence of Wall Interactions in the Absence of	Axial
Inhomogeneity	84
4.1. Theoretical Formulation	84
4.2. Kinetics of Adsorption and Desorption	90
4.2.1. Fast Adsorption and Desorption: the Chromatographic Limit	91
4.3. Applications	96
4.3.1. Influence of Wall Interactions	96
4.3.1.1. Uniform Wall Interactions	96
4.3.1.2. Nonuniform Wall Interactions	98
4.3.2. Influence of Inhomogeneous Flow Fields	100
4.3.2.1. Pressure-driven Flow in Various Cross-Sections	105
4.3.2.2. Electrokinetic Flow with Finite Debye Layers	106
4.3.2.3. Shear Flow	107
4.3.3. Band broadening in chromatography	109
4.4. Numerical Comparisons	111
4.4.1. Slow Irreversible Adsorption in a Circular Capillary	111
4.4.1.1. Theory of Slow Irreversible Adsorption	111
4.4.1.2. Numerical Methods	114
4.4.1.3. Numerical Results	114

3.4.1. Results for Slowly Varying Wall Zeta Potential: Comparison with Lubrication

4.4.2. Dispersion in a rectangular channel with wall interaction	115
4.4.2.1. Test Problems	116
4.4.2.2. Numerical Methods	117
4.4.2.3. Metrics for Cases A and B	118
4.4.2.4. Numerical Results for Case A	118
4.4.2.5. Numerical Results for Case B	124
4.5. Summary	135
Chapter 5. Dispersion in the Presence of Wall Interactions in the Presence of Axial	
Inhomogeneity	136
5.1. Introduction	136
5.2. Dispersion in Slowly Varying Channels	138
5.3. Dispersion in an Inhomogeneous Electroosmotic Flow	145
5.3.1. Dispersion under an Axial Distribution of Zeta Potential in Absence of	
Adsorption-desorption	147
5.4. Numerical Comparisons	148
5.4.1. The Test Problem	148
5.4.2. Numerical Methods	149
5.4.3. Numerical Results	149
5.5. Summary	155
Chapter 6. Conclusions	156
References	160
Appendix A. Derivation of Equation (5.15)	167

List of Tables

2.1	Solutions of Poisson-Boltzmann Equation in Various Geometries	32
4.1	Pressure-driven flow Distribution for Various Geometries	101
4.2	Functions Ψ and χ for Pressure-driven Flow in Various Geometries	108
4.3	Shape Function and coefficients for shear-driven flow F_s in a Plane	
	Channel	108
4.4	Resistance to Mass Transfer in the Mobile Phase in Chromatographic	
	Separations	110
4.5	Dependence of the coefficients $\overline{\chi_{\kappa}F_{\kappa}}$ and $\overline{\psi}F_{\kappa}$ on the dimensionless Debye	9
	Hückel Parameter $\kappa' = \frac{2b}{\lambda_D}$ in Case B.	126

List of Figures

1.1	Schematic of a Microfluidic Chip for Separation	22
1.2	Schematic of a Capillary Zone Electrophoresis Setup	23
1.3	Illustration of Electroosmosis and Electrophoresis	24
3.1	Geometry of the rectangular channel showing a typical cross-section	
	ABCD	47
3.2	Illustration of Cases A, B and C	58
3.3	The staggered grid for numerical solution	62
3.4	Electroosmotic mobility for Case A	66
3.5	Pressure gradient (π_*) as a function of $x/2b$ for Case B	67
3.6	Electroosmotic mobility for Cases B and C	68
3.7	Pressure Gradient with $\lambda = L = 40b$ in Case D	69
3.8	Pressure Gradient with $\lambda = L/10 = 4b$ in Case D	70
3.9	Theoretical and numerical $u(y, z)$ for $\lambda = L = 40b$	71
3.10	Theoretical and numerical $u(y,z)$ for $\lambda = L/10 = 4b$ in Case D	72
3.11	Theoretical and numerical $u(0, z)$ and $u_p(0, z)$ for $\lambda = L = 40b$ in Case D	73
3.12	Theoretical and numerical $u(0,z)$ and $u_p(0,z)$ for $\lambda = L/10 = 4b$ in Case	
	D	74

3.13	$u_p(0,z)$ for different amplitudes $(\Delta \zeta/\zeta_0)$ in Case D	75
3.14	Numerical $u(y = 0, z)$ for $\lambda = L = 40b$ in Case E compared with	
	lubrication and parallel-plate theory	77
3.15	Numerical $u(y = 0, z)$ for $\lambda = L/10 = 4b$ in Case E compared with	
	lubrication and parallel-plate theory	78
3.16	Numerical $u(y = 0, z)$ for $\lambda = 2b$ in Case E compared with lubrication	
	and parallel-plate theory	79
3.17	Numerical $u(y = 0, z)$ for $\lambda = 2b/3$ in Case E compared with lubrication	
	and parallel-plate theory	80
3.18	Numerical $u(y = 0, z)$ for $\lambda = 2b/12$ in Case E compared with lubrication	L
	and parallel-plate theory	81
4.1	Shear-Driven Chromatography and AC Electroosmotic Micro-pumping	102
4.2	Shape function χ for a square	103
4.3	Flow Profiles and Shape Functions for a Trapezoid	104
4.4	Fraction of solute in a Cylindrical Capillary vs. Time	119
4.5	Logarithmic Rate of Solute Loss vs. Adsorption Rate Constant in a	
	cylindrical capillary	120
4.6	Speed of Center of Mass vs. Adsorption Rate Constant in a Cylindrical	
	Capillary	121
4.7	Effective Dispersion Coefficient vs. adsorption rate constant in a	
	cylindrical capillary	122
4.8	Migration Speed vs. Time in Case A	127

4.9	Effective Dispersion Coefficient vs. Time in Case A	128
4.10	Migration Speed vs. Adsorption Rate Constant in Case A	129
4.11	Effective Dispersion Coefficient vs. Adsorption Rate Constant in Case A	130
4.12	Concentration Distribution in Case A showing transverse variations	131
4.13	Formation of Secondary Peaks in Case A	132
4.14	Migration Speed vs. Debye Hückel Parameter in Case B	133
4.15	Effective Dispersion Coefficient vs. Debye Hückel Parameter in Case B	134
5.1	Geometry of the axially variable channel	137
5.2	Effective dispersion coefficient vs. time for three different values of Λ	151
5.3	Effective dispersion coefficient vs. time for three different values of $\Delta \zeta$	152
5.4	Concentration distribution at various times for $\lambda = L/5 = 51.2b$ and	
	$\Delta \zeta / \zeta_0 = 0.75$	153
5.5	Concentration of solute in the liquid and adsorbed state showing	
	transverse variations for $\lambda = L/5 = 51.2b$ and $\Delta \zeta/\zeta_0 = 0.75$	154

CHAPTER 1

Introduction

1.1. Electroosmosis and Electrophoresis

When a solid surface comes in contact with a liquid containing free ions, it often acquires a charge on its surface through charge transfer mechanisms like ionization of surface groups and ion adsorption [1]. If an external electric field is applied to the liquid confined within such a solid surface, a motion is induced in the liquid. This phenomenon is known as electroosmosis, or electroosmotic flow. On the other hand, if a charged solid particle is bounded by the liquid medium, then the applied external electric field causes a motion of the particle relative to the liquid. This phenomenon is known as electrophoresis. Both electroosmosis and electrophoresis fall under the broader category of electrokinetic phenomena which deal with the interaction between electric field and fluid flow at an interface between a solid substrate and an electrolyte. Other manifestations of electrokinetic phenomena are the streaming potential and the sedimentation potential [2].

1.2. Electrokinetic Phenomena in Microfluidic Separation Systems

Applications based on the phenomenon of electroosmosis and electrophoresis play an important role in separation science -the science of separating, identifying and characterizing the components of chemical mixtures. Progress in separation science has been a key driver behind recent developments in biology, medicine, forensics and environmental sciences [3, 4]. Macro-scale applications like slab-gel-electrophoresis (e.g. for analysis of serum in clinical pathology) have existed for decades [5].Progress in our understanding of biological phenomena at the cellular level and molecular level has evolved hand in hand with progress in separation technology. Devices known as microfluidic chips which can perform biochemical tasks like synthesis, analysis and reactions on the micron scale with nanoliters of sample volumes [6] are receiving increasing attention in research and industry. The 'lab-on-a-chip' concept (see for example [7] and the references therein) of integrating all these tasks with a high degree of automation on a single microfluidic chip containing the required complex network of micron-sized channels, sensors, actuators, valves, junctions and reservoirs has now passed the development phase. 'Labs-on-chips' are now being manufactured commercially by companies like Agilent Technologies, Beckman Coulter, Handylab and Microchip Biotechnologies. Such miniaturization and parallelization of biochemical steps, it is hoped, will in the near future vastly speed up procedures such as sequencing of genes in much the same way microelectronics led to the era of ubiquitous computing.

Figure 1.1 shows the schematic of a microfluidic chip that can be used for performing separations. The reservoirs for the buffer (electrolyte) are connected by a microchannel which intersects the microchannel connecting the sample reservoirs. The shorter of the two microchannels is used for injecting the sample into the longer microchannel where the separation can takes place by mechanisms such as CE and CEC. The sectional view reveals that the reservoirs and the channels are patterned out of two different substrates and bonded together. Common materials used for microfluidic device fabrications are glass and poly(dimethylsiloxane) or PDMS and the common fabrication methods are often based on lithography [8].

Electroosmotic flow is often the preferred method for the transport of the samples, reagents and buffers in a microfluidic circuit (unlike in fluidic/hydraulic circuits where flows

are typically driven by pressure). This is because the pressure difference (Δp) required to hydraulically drive a given flow rate through a capillary scales more adversely $(\Delta p \propto d^{-4})$ with capillary diameter (d) than the voltage difference (ΔV) required to drive the same flow rate electroosmotically $(\Delta V \propto d^{-2})$. Additionally, electroosmotic flows have the much desirable shear-free plug-type profiles across the cross-section of a microfluidic channel that reduces the unwanted effects of shear-induced (Taylor-Aris) dispersion [9, 10] in separation processes. Pressure-driven separation processes (e.g. Liquid Chromatography) have lower resolution than their electric field driven counterparts (e.g. Capillary Electrochromatography (CEC)) because of Taylor-Aris dispersion [9, 10] that causes broadening of solute bands [11]. Moreover, the miniaturization of the microfluidic chip is simplified by the use of a common voltage supply to actuate injection valves, drive flow (EOF) and separate species (e.g. CE/CEC and mass spectroscopy)[8].

Capillary electrophoresis (CE) is an electrophoretic separation technique that introduces the sample to be analyzed in the form of a sharp band into an EOF established in a capillary. A bench-top or conventional setup for CE is shown schematically in Figure 1.2. The capillary for CE is typically of diameter $25 - 75 \,\mu\text{m}$ and length $10 - 100 \,\text{cm}$ and usually made of fused silica. The buffer fills the capillary and the two reservoirs where the electrodes from a high voltage supply are introduced. Typical electric fields are of the order of $0.1 - 1 \,\text{kV/cm}$. A detector (usually of the UV-ray absorption type) is placed at one end of the capillary. Each chemical constituent of the sample acquires a different electrical charge from the buffer and therefore, acquires a different electrophoretic velocity relative to the electroosmotic flow depending on the molecular size, shape and level of ionization of the various chemical groups on its surface. Thus, the sample splits into several bands, each moving with a different speed, and therefore, reaching the detector at a different time. Capillary Zone electrophoresis has been used with higher resolution, higher speeds, greater automation and lower sample volumes in all the traditional applications of slab gel electrophoresis (where the electrophoretic motion took place within the pores of a gel instead of a capillary). The application of CE include identification, characterization and separation of proteins, sequencing of nucleic acids, separation of enantiomers and identification of functional groups and inorganic ions. For example, CE was used in the sequencing of the DNA molecule in the latter stages of the Human Genome Project [12].

Capillary electrochromatography (CEC), a chromatographic separation technique of considerable promise uses electroosmotic flow to transport the sample past an adsorbent surface (in the form of a packed bed in packed-bed CEC or as coating on the walls in open-tubular CEC), the retention times on the adsorbent surface of different chemical constituents in the sample, being responsible for the separation. A CE setup can be modified in the laboratory into a setup for open-tubular CEC [13]. Bench-top CEC and CE systems can also be purchased from companies like Agilent Technologies, Beckman Coulter and Analytical Technology.

1.3. Key Physical concepts

A charged surface attracts the counterions (ions of opposite charge) and repels the coions (ions of like charge) in the electrolyte creating a thin layer of net opposite charge next to the surface. This is known as the electrical double layer (EDL) or Debye layer. When an external field is applied, the momentum imparted by the electric field to the charges in the EDL is transmitted to the neutral fluid outside the EDL through the effect of viscosity. If the fluid phase is mobile, a motion is induced in the liquid. This would be the case if the solid phase is in the form of walls confining an electrolyte. This is the basic mechanism of electroosmosis in a channel and is illustrated in Figure 1.3(a). The ratio of the mean velocity of the net flow (\mathbf{v}_{eof}) in the confined electrolyte to the electric field (\mathbf{E}_0) is known as the electroosmotic mobility (μ_{eof}) . If the solid phase is mobile (e.g. a solid particle suspended in the electrolyte), the charge on its surface, partially shielded by the EDL will cause it to acquire a motion (opposed by a viscous drag induced by its own motion as well as by the electrical body forces in its double layer [2]) with a constant terminal velocity \mathbf{v}_{ep} . This is the basic mechanism of electrophoresis of a particle and is illustrated in Figure 1.3(b). The ratio of \mathbf{v}_{ep} to the applied electric field (\mathbf{E}_0) is known as the electrophoretic mobility (μ_{ep}) of the particle.

1.4. Effect of Inhomogeneities in EOF and Wall Interactions on Separations

If the width of a channel is much larger than the characteristic thickness of the EDL and all properties are uniform, the EOF in the channel is to a good approximation a 'plug flow' or uniform flow [1]. However, there are situations when the EOF is axially and radially inhomogeneous, e.g. as a consequence of variation of zeta potential on the walls and/or microchannel cross-section [7], or due to finite Debye layer effects [14].

In the case of spatially varying zeta potential, exact analytical solutions of the fluid flow equations are not available except for certain special geometries. One way of predicting the resultant electroosmotic flow theoretically is to utilize the lubrication approximation [15], but this requires the characteristic scale of axial variation to be large compared to the channel width. Numerical solution of the equations governing fluid flow is another alternative which is more versatile, as it can handle slow as well as fast variations. However, it can be expensive in terms of computation time and memory because a microchannel typically has a large length to width ratio. In this dissertation, we will simulate numerically some representative flows involving wall zeta potential variation in a channel of rectangular cross-section and test the accuracy of predictions based on the lubrication approximation by comparison with numerical results. We will also demonstrate that the lubrication approximation fails when the zeta potential varies on a scale smaller than channel width and that in this limit, an analytical approximation is possible on the basis of a theory developed by Ajdari [16].

While an inert solute in a uniform 'plug' flow spreads solely on account of molecular diffusion, presence of inhomogeneities in the flow leads to enhanced spreading of solute bands by the Taylor-Aris dispersion mechanism [9, 10]. Drawing from the classic analysis and experiment of Taylor [9], we can conclude that the effective diffusivity in this situation can be many times the molecular diffusivity of the solute in the buffer, and is, in fact, inversely proportional to the molecular diffusivity. The problem of solute transport under non-ideal electroosmosis conditions in microfluidic devices [17] constitutes one of the motivations for the work described in this dissertation. However, it is more general in scope as it can account for any axially variable flows and cross-sectional shape changes [16, 18], provided they take place on a slow time and spatial scale in the axial direction.

Adsorption of proteins and peptides to channel walls is one of the most pernicious problems in CE separations [19]. This problem is considered to arise from electrostatic interaction between the protein molecule which usually carries a net positive charge and the capillary wall surface, which carries a net negative charge at the buffer pH values used in CE separations. However, details of the adsorption kinetics is not well understood in the literature. Wall adsorption have been shown to cause sample loss in the analysis of certain proteins [20], suggesting a slow irreversible wall reaction. But the presence of a fast reversible interaction has also been pointed out to be a plausible explanation for certain experimental observations [19] (e.g. the slow movement of peaks of the protein Rhodamine B in [19]).



Figure 1.1: Schematic of separation and injection channels on a Microfluidic Chip



Figure 1.2: Schematic of a Conventional Capillary Zone Electrophoresis Setup (based on [7])



(b) Electrophoresis

Figure 1.3: Illustration of Electroosmosis and Electrophoresis

Following excerpt from the abstract of a talk on adsorption of the protein Lactoglobulin to be presented later this year by Rabe et al [21] illustrates the complexity of the adsorption mechanism, even for a single protein :

" Important experimental observations were ... transition to an almost irreversibly bound state of the protein in the long term. Furthermore,... adsorbed proteins abruptly change their desorption behavior from irreversible to reversible when a critical surface coverage is reached."

In this situation, models for solute transport that incorporate specific empirical laws of the wall interaction kinetics at an early stage of the analysis is expected to lack versatility and predictive capability. This is the case, with most models [22, 23, 24] in the literature that utilize approaches based on the well-established theory of chromatography [25] to study solute dispersion in the protein adsorption problem. Further, the theory of chromatography is inaccurate if adsorption and desorption are not fast enough for equilibrium to be established during the time of separation. The approach adopted in this work is able to treat both fast and slow adsorption-desorption kinetics.

On the other hand, the working principle of a CEC separation involves a fast and reversible exchange of solute between the mobile phase and the stationary phase, while the solute is transferred across the separation channel due to electrophoresis and electroosmosis: indeed, CEC is known as a 'hybrid technique' combining the principles of adsorption chromatography [26] and CE [27]. Each constituent of the mixture being analyzed spends a different fraction of the analysis time in an immobile adsorbed state on the wall and therefore moves with a different effective speed. However, the more retained solute also spreads over a wider zone, adversely affecting the resolution. Like Taylor-Aris dispersion, this mechanism

results in higher dispersion for solutes with lower molecular diffusivity and the extent of dispersion increases with the flow rate [28, 29]. Dispersion in CEC has been studied in the literature mostly from the perspective of small departures from equilibrium [25]. It has been argued, however, that some anomalous situations in experimental practice may be due to slow wall interactions, far from the state of equilibrium [26, 30].

We summarize now, the motivation to pursue this work as presented in this section. It is one of our motivations to predict inhomogeneous flow fields in electroosmosis, as they cause enhanced dispersion in separations. A common cause is the variation of the surface charge or the electric potential acquired by the wall (known as zeta potential) at different points of the capillary, which will be investigated with numerical and approximate analytical tools. Dispersion of solutes in microchannels under inhomogeneous flow fields and with adsorptiondesorption on walls are studied, when both effects are present simultaneously, as they occur in CEC and CE practice [**31**], since they reinforce one another. Our analysis is kept general with respect to the shape of the microchannel in order to address current and hopefully future developments in microfluidic chip design and fabrication for separations [**6**]. We also treat wall interactions by an approach that is appropriate for studying dispersion in both CE and CEC. The small width of a microchannel is taken advantage of, to formulate a simpler and less computationally intensive numerical tool than direct simulation.

1.5. Objectives

The following are the specific objectives of the work described in this thesis:

(i) to calculate the electroosmotic flow (EOF) in a straight micro-channel of rectangular cross-section numerically for several representative problems where the wall zeta potential has a specified spatial variation.

- (ii) to test the accuracy of predictions based on the lubrication approximation [15] of the EOF against the numerical results. In particular, to vary the characteristic scale for axial variation of zeta potential from large (lubrication theory expected to be accurate) to small (lubrication theory expected to be inaccurate) values to find the domain of applicability of lubrication theory.
- (iii) to test the accuracy of an approximation based on the Stokes limit solution of EOF between parallel plates (parallel-plate theory) [18] against the numerical results. In particular, to vary the characteristic scale for axial variation of zeta potential from large (parallel-plate theory expected to be inaccurate) to small (parallel-plate theory expected to be accurate) values to find the domain of applicability of the parallel-plate theory.
- (iv) to develop an asymptotic theory for the problem of the transport of a solute in a microchannel of arbitrary cross-section, under an axially homogeneous flow field, and in presence of adsorption-desorption on the wall, when all axial and temporal variations are slow.
- (v) to extend the asymptotic theory of solute transport and adsorption-desorption to axially variable cross-sections and axially inhomogeneous flow fields, when all axial and temporal variations are slow.
- (vi) to numerically solve the complete problem of solute dispersion in some situations relevant to microfluidic separations like CE and CEC, that involve adsorptiondesorption and inhomogeneous electroosmotic flow in rectangular micro and nanochannels with or without adsorption-desorption on the wall, in presence or in absence of axially variable flows

(vii) to compare the results from the direct numerical solution to those from the developed asymptotic theory of transport, in order to assess the accuracy of the latter.

CHAPTER 2

Electroosmotic Flow and Dispersion in Microfluidic Separation Systems: Fundamentals

The physical processes in the electrical double layer (EDL) that give rise to electroosmotic flow (EOF) involve complex interaction between fluid mechanics, electrical, thermal and chemical effects. The fluid flow can be described by the incompressible Navier Stokes Equations with a volume density of electrical forces $\mathbf{f}_{\mathbf{e}} = -\rho_e \nabla \phi$. Here ρ_e is the net electric charge density and ϕ is the electric potential. The inertia terms can be neglected in a wide variety of circumstances and the flow description by Stokes Equations may be adequate [6]. The potential ϕ can be related to the charge density through the Gauss Law [32] of electrostatics:

(2.1)
$$\kappa \nabla^2 \phi = -4\pi \rho_e.$$

Here, κ is the permittivity of the liquid (in CGS units). The net charge density can be calculated from the individual concentration (number density per volume) of the ionic species in the electrolyte. Here, we assume for algebraic simplicity that the electrolyte contains only two species: a monovalent cation with concentration n^+ and a monovalent anion with concentration n^- . For a full treatment with arbitrary number of species with arbitrary valences, see [7]. Then, $\rho_e = (n^+ - n^-)e$, where e is the electronic charge. The concentration of each species can be calculated from the conservation equations:

(2.2)
$$\frac{\partial n^{\pm}}{\partial t} + \nabla \cdot \mathbf{j}^{\pm} = 0$$

where \mathbf{j}^{\pm} , the species flux vector can be modeled by the Nernst-Planck equation for ion transport [33]:

(2.3)
$$\mathbf{j}^{\pm} = \mp v^{\pm} e n^{\pm} \nabla \phi - D^{\pm} \nabla n^{\pm} + n^{\pm} \mathbf{u}.$$

Here, v is the ionic mobility. From statistical thermodynamical considerations, it can be shown $D/v = k_B T$ (the Einstein relation) where k_B is the Boltzmann constant and T is the absolute temperature.

The boundary conditions for these equations on the interface are $\mathbf{j}^{\pm} \cdot \hat{\mathbf{n}} = 0$, meaning that the interface is impervious to the flux of the species and $\phi = \zeta$. Here, ζ is the zeta potential of the interface which is the potential on the 'shear surface' in the EDL (methods of measuring ζ may be found, for example, in [34]).

2.1. Gouy Chapman Model of the EDL

The Gouy Chapman model of the EDL is a steady state model valid under equilibrium conditions (no fluid flow and no electric field). It can be concluded under those circumstances from Equations (2.1),(2.2),(2.3) and the boundary condition $\mathbf{j}^{\pm} \cdot \hat{\mathbf{n}} = 0$ that the ionic number density is governed by:

(2.4)
$$n^{\pm} = n(\infty) \exp\left(\mp \frac{e\phi}{k_B T}\right)$$

where n_{∞} is the charge density far away from the surface (same for cations and anions since bulk electrolyte is neutral). Then, $\rho_e = (n^+ - n^-)e$ can be calculated from Equation (2.4) and used in the right hand side of Equation (2.1) to obtain the following non-linear equation for the electrical potential :

(2.5)
$$\nabla^2 \phi = \frac{8\pi n(\infty)e}{\kappa} \sinh\left(\frac{e\phi}{k_BT}\right)$$

This is known as Poisson-Boltzmann Equation and was used by Gouy [35] and Chapman [36] in their investigation of the EDL.

2.2. The Debye-Hückel Approximation

The Debye-Hückel approximation is a linearization of the function on the right hand side of the Poisson-Boltzmann Equation (2.5) valid in the low electrostatic potential (LEP) limit [18] i.e. when $\kappa |\zeta| / (k_B T) \ll 1$. Then, Equation (2.5) simplifies to:

(2.6)
$$\nabla^2 \phi - \mathcal{K}^2 \phi = 0$$

where:

(2.7)
$$\mathcal{K} = 1/\lambda_D = \left[\frac{8\pi e^2 n(\infty)}{\kappa k_B T}\right]^{\frac{1}{2}}.$$

The constant \mathcal{K} has the units of inverse length and defines a length scale λ_D known as the Debye-length or Debye-shielding length. The solution to Equation (2.6) for a charged plate at potential ζ is $\phi = \zeta \exp(-z/\lambda_D)$, where z is the co-ordinate normal to the plate.

The potential field decreases by a factor e (37%) at a distance λ_D from the plate. This gives us the physical conclusion that λ_D characterizes how well a given electrolyte is 'shielded'

Configuration	$\frac{\phi}{\zeta}$
Infinite Plane	$\exp\left(-\mathcal{K}y\right)$
Infinite Cylindrical Capillary	$\cosh\left(\mathcal{K}y\right)/\cosh\left(\mathcal{K}b\right)$
Narrow Slit	$I_0(\mathcal{K}r)/I_0(\mathcal{K}a)$

Table 2.1: Solutions of the Poisson-Boltzmann Equation (Equation (2.6) with $\phi(y = 0) = \zeta$) in various geometries. In the first configuration, y is measured from the plane. In the second configuration, 2b is the width of the slit between two parallel planes; y is the co-ordinate normal to the plane with origin at a point halfway between the planes. In the third configuration, a is the radius of capillary , r is the radial co-ordinate measured from the axis of symmetry of the capillary and I_0 is the modified Bessel function of the first kind and of order zero.

from the effect of the surface charge acquired by the plate. It also characterizes the thickness of the EDL. The surface charge density (σ) on the plate can be calculated by the relationship $\kappa \frac{\partial \phi}{\partial z}|_{z=0} = -4\pi\sigma$, giving $\sigma = \kappa \zeta/4\pi\lambda_D$. One can conclude that higher the thermal energy (k_BT) of the ions and/or electrical permittivity (κ) of the electrolytic medium, and lower the number density of free ions in the bulk of electrolytic solution, more diffuse the EDL is (larger λ_D). The condition for the above linearization to be valid is often met marginally, e.g. at room temperature the $k_BT/e \simeq 30 \ mV$ and for silica substrate $\zeta \simeq 100 \ mV$. However, this linearization gives fairly accurate results, well beyond its range of formal validity [7].

Equation (2.6) can be solved for other geometries (infinite cylindrical capillary with uniform charge on its walls and the narrow slit between two uniformly charged plates) with the electric potential ζ on the surface(s) assumed to be specified. The solutions are tabulated in Table 2.2 which is constructed from Equation (12) of [7]. A solution for rectangular capillary, a common microfluidic configuration has been calculated by Andreev and Lisin [37].

2.3. Solution for Flow in EDL under External Electric Field

The Gouy-Chapman theory discussed earlier is valid in the absence of an external electric field and fluid velocity field and cannot, in general, be used in non-equilibrium situations. However, in many situations, the electric field and the fluid velocity develop along the surfaces of constant net charge density ρ_e , which allows us to use the equilibrium charge distribution calculated from the Gouy-Chapman theory. For example, this is the case a uniform electric field strength E_0 is applied parallel to uniformly charged wall(s) in a semi-infinite media or in long straight channels of cylindrical, plane or rectangular cross-sectional shape. In all these above cases, the only non-zero component of fluid velocity u is directed parallel to the wall(s) is determined by the balance of viscous and electrical body force (assuming zero pressure gradient) in the fluid flow equations, as follows:

(2.8)
$$\mu \nabla^2 u + \rho_e E_0 = 0.$$

Using Equation (2.1) for ρ_e this becomes:

(2.9)
$$\mu \nabla^2 u - \frac{\kappa E_0}{4\pi} \nabla^2 \phi = 0.$$

If the ζ potential is axially invariant, this equation with the no-slip boundary condition u = 0 on the wall can be integrated twice to get the solution [7, 1, 2, 6].

(2.10)
$$u = \frac{\kappa E_0}{4\pi\mu} \left[\phi - \zeta\right]$$

where ϕ can be calculated from Gouy Chapman theory. If Debye-Hückel approximation is valid, then the values of ϕ from Table 2.2 can be used to get the velocity profile [7].

2.4. The Thin Debye Layer (TDL) Limit for EOF

The characteristic thickness of the EDL ($\lambda_D \sim 1 - 10 \,\mathrm{nm}$) is exceedingly small compared to a linear dimension of a microfluidic channel ($a \sim 10 - 100 \,\mu\mathrm{m}$). So, the EDL forms a thin boundary layer near the walls of the channel where the electrical forces are confined. In this 'inner region' the charge, electrical potential and flow can be calculated by the approach described in the last two sections. Outside this layer, the liquid is charge neutral, though electrically conducting. Thus, the fluid motion outside the EDL can be represented by the Navier Stokes equations, but with no electrical body force term. In terms of the theory of matched asymptotic methods [**38**], a matching condition between the 'outer' problem and the 'inner' (EDL) problem is necessary to solve the flow field in the complete problem. In the limit when the EDL is infinitely thin, only the 'outer problem' needs to be solved and this 'matching condition' for velocity can be used as the velocity boundary condition. On a wall at y = 0 moving with velocity \mathbf{U}_w , the standard 'no-slip condition' $\mathbf{u}(y = 0) - \mathbf{U}_w = 0$ of fluid mechanics, can, thus be replaced by the following Helmholtz-Smoluchowski (HS) slip condition:

(2.11)
$$\mathbf{u}(y=0) - \mathbf{U}_w = \mathbf{u}_{\mathbf{e}} = -\frac{\kappa \zeta \mathbf{E}}{4\pi\mu}$$

The electric field $\mathbf{E} = -\nabla \phi$ is calculated by solving Laplace's equation for electric potential ϕ with an insulating boundary condition $E \cdot n = 0$ indicating no current flow through the wall.

2.5. The Plug Flow Solution of EOF

The electroosmotic flow in an infinitely long channel with constant cross-sectional area subject to zero pressure difference and an applied electric field (E_0) in the axial direction is a parallel and irrotational flow with the axial component $u = u_e$ since there is no source of shear outside the EDL, where u_e is the HS slip velocity in (2.11). Therefore,

(2.12)
$$u = -\frac{\kappa \zeta E_0}{4\pi\mu}.$$

In the above, zeta potential and all material properties in the pre-factor multiplying E_0 are assumed to be constant. This solution is a special case of a general class of exact solutions (pointed out by [**39**] in context of electrophoresis of particles of arbitrary shape) of the Navier Stokes Equation with the HS slip boundary conditions, that are characterized by irrotationality and proportionality between velocity and electric fields. This flow profile is commonly known as the plug profile of EOF as distinct from the parabolic profiles of pressure driven flows. A desirable feature of this profile is that it can transport bands of solutes in separation processes like CE without shear-induced dispersion [**9**, **10**].

2.6. Flows with Axial Variation

The flow-field given by (2.12) is not correct if the zeta potential (or any of the other material constants in Equation (2.12)) is spatially varying. In fact, persisting with Equation (2.12) when zeta potential is varying axially would lead to the un-physical conclusion that volume flow rates across cross-sections at different axial locations ($\bar{u}A$) are unequal. In reality internal pressure gradients are induced that causes the flow at locations with high zeta potential to be slowed down near the axis and the flow at locations with low zeta potential to be speeded up near the axis, thus preserving the continuity of the fluid. Thus, the observed flow field is both axially and radially inhomogeneous and cannot be represented by Equation (2.12). The spatial variation in zeta potential can be introduced in an electroosmotic flow :

- (i) by accidental inhomogeneities on the walls of the channel [40],
- (ii) by adsorption of small amounts of sample to the wall in an axially inhomogeneous manner in an EOF based separation process like CE [20, 41, 31]
- (iii) by intentional patterning of surface charges on the wall, to serve purposes like promotion of mixing, control of dispersion in turns and bends [42, 43, 44].
- (iv) by the inhomogeneous modification of surface charge through absorption of solutes from separation processes like CE [20, 31].

. These situations can be considered the motivation for finding solutions to EOF under arbitrary variation in wall zeta potential.

2.6.1. Exact Solutions

Anderson [45] has solved the problem of Stokes flow (Re = 0) in cylindrical geometry under arbitrary axial variation in the wall zeta potential. He considered a very long capillary of length (L) and radius a ($L \gg a$) subject to an axial zeta potential variation $\zeta = \zeta(x)$. There is an electrical potential drop $\Delta V = EL$ over the capillary length and the pressure drop across the capillary was zero. The Stokes equation was expressed in terms of the streamfunction Ψ and solved using Fourier transform methods. Anderson's solution is $\mathbf{u} = u\hat{\mathbf{x}} + v\hat{\mathbf{r}}$ where xand r are the axial and radial coordinates and $u = -\frac{1}{r}\frac{\partial\Psi}{\partial r}$ and $v = \frac{\partial\Psi}{\partial x}$ and Ψ is given by:

(2.13)
$$\Psi = \frac{\kappa E_0}{4\pi\mu} \left[\frac{r^2}{2} \langle \zeta \rangle - 2\sum_{m=1}^{\infty} a_m^c(r) \cos\left(\frac{2m\pi x}{L}\right) - 2\sum_{m=1}^{\infty} a_m^s(r) \sin\left(\frac{2m\pi x}{L}\right) \right]$$
where:

(2.14)
$$\frac{a_m^c}{\hat{\zeta}_m^c} = \frac{a_m^s}{\hat{\zeta}_m^s} = \frac{arI_0(\alpha_m)I_1(\alpha_m r/a) - r^2I_1(\alpha_m)I_0(\alpha_m r/a)}{\alpha_m I_1^2(\alpha_m) + 2I_0(\alpha_m)I_1(\alpha_m) - \alpha_m I_0^2(\alpha_m)}$$

Here, $\alpha_m = 2\pi ma/L$ and I_n is the modified Bessel function of first kind and integral order *n*. The $\hat{\zeta}_m^c$ and $\hat{\zeta}_m^s$ are the cosine and sine transforms of the zeta potential defined by $L^{-1} \int_0^L \zeta(x) \cos(\alpha_m r/a) dx$ and $L^{-1} \int_0^L \zeta(x) \sin(\alpha_m r/a) dx$ and $\langle \zeta \rangle$ denotes the axial average $L^{-1} \int_0^L \zeta dx$. A remarkable conclusion from this work is the following formula for the crosssectionally averaged axial velocity:

(2.15)
$$\overline{u} = -\frac{\kappa \langle \zeta \rangle E_0}{4\pi\mu}$$

meaning that the flow rate through a capillary with axially varying zeta potential ζ is the same as that of a capillary subject to a uniform zeta potential of $\langle \zeta \rangle$.

Long, Stone and Ajdari [46] has solved the EOF problem for parallel plate geometry. This solution will be discussed with respect to a single wavelength of variation in zeta potential (after [18]) in Section 3.1.3, as this is relevant to the numerical simulation of flow in rectangular channels.

Capillaries with rectangular cross-section are common in experiments on electroosmotic flow [47, 17] and microfluidic applications [6]. However, unlike the geometries like circular capillaries [45] and parallel plates [18], exact solutions to the EOF problem under TDL approximation for arbitrary $\zeta(x)$ is not available in the literature for this geometry. This may be related to the fact that the traditional solution procedure involving solution of a biharmonic equation for the Stokesian streamfunction [45, 18] require two-dimensionality or circular symmetry and the flow in rectangular channels is three-dimensional. The theoretical model of [37] has dealt with the simplified situation of uniform but unequal zeta potential distribution on the walls of a rectangular channel, when the flow is two-dimensional. The theoretical and numerical results of Conlisk et al [48] in rectangular geometry proceed with the Debye-Hückel approximation, but without the assumption of infinitely thin Debye layer. Conlisk et al [48] have derived a one-dimensional approximation for the velocity field valid when the aspect ratio of the channel is small.

2.6.2. Solution in the Lubrication Limit

The problem of EOF in the TDL limit under arbitrary zeta potential becomes tractable for straight channels of arbitrary cross-sectional shape through the lubrication approximation [49], provided the variation of cross-section and zeta potential takes place on a length scale much larger than a typical linear dimension of the channel cross-section. This has been done by Ghosal [15] and will be discussed in Section 3.1.2. Long, Stone and Ajdari [46] has also used the lubrication approximation to study the effect of surface defects in planar and cylindrical capillaries.

2.7. Consequences of Axial Variation of Zeta Potential in CE channels

Axial zeta potential variation in CE channels are usually caused by inhomogeneities on the wall or absorption of solutes are has three principal effects:

(a) Elution time delays: A simple expression for the velocity of a band(v) in CE is $(\mu_{ep} + \mu_{eo})E_0$, where μ_{ep} is the electrophoretic mobility and μ_{eo} is the electroosmotic mobility. From Equation (2.15) it can be concluded that the μ_{eo} is lowered as sample adsorption lowers $\langle \zeta \rangle$. An analysis by Ghosal [50] based on this idea is in quantitative agreement with the experimental data of Towns and Regnier [51, 20].

- (b) Shear-induced dispersion: The non-uniformity of EOF under variable zeta potentials leads to enhanced spreading of bands by the Taylor-Aris dispersion [9, 10] mechanism, lowering the resolution of separations.
- (c) Asymmetric peaks: The bands are often asymmetric with peaks lying usually on the leading side of the centroid (negative skewness). The asymmetry effect can be accounted for by considering the dynamics of adsorption processes that modify the zeta potential [31]. An asymptotic model of this problem connecting the mobile phase concentration and adsorbed surface concentration has been formulated by Ghosal [31] and the full numerical problem has been solved in circular geometry [52]. Numerical calculations in [52] suggest the following mechanism: Wall adsorption usually lowers the zeta potential of regions passed by the peak and in a region of lowered zeta potential, near wall particles are convected at a slower speed than they are at a region of unaffected zeta potential, thus the wall adsorption is more effective in removing material downstream of the plug than upstream of it. Peak asymmetry can also originate from nonuniform electro-migration [53] or the shape of the wall adsorption isotherm [54]; however, these effects vanish with lower sample concentrations.

2.8. Dispersion in Microfluidic Systems

Excessive spreading or dispersion of a band of solute has an undesirable effect on the efficiency of CE and CEC separations. Other than molecular diffusion, there are various sources of dispersion in a microfluidic separation systems like dispersion induced by turns in a microchannel [55, 56], Joule heating [57, 58, 59] and high sample concentration affecting buffer conductivity [60]. Fairly detailed reviews of these dispersion modes can be found in

[7, 61]. In this work, we will concentrate on dispersion phenomena that originate from the hydrodynamics and surface adsorption effects in microfluidic channels .

2.9. Taylor-Aris Dispersion with Inert Walls

The mathematical study of the spreading of solutes under a pressure-driven flow in small diameter pipes w as initiated by Taylor [9]. He concluded that the solute advects with the mean speed of the flow and spreads with an effective diffusivity that is inversely proportional to the molecular diffusion coefficient. Taylor's analysis is valid in the long time limit (in comparison to the characteristic radial diffusion time) and when axial spreading by molecular diffusion is negligible. Aris [10] put Taylor's work under a more general mathematical framework, that later became known as the Method of Moments. In the Method of Moments, a sequence of two dimensional initial-boundary-value problems are solved for moments in the axial direction at each radial location. These integral quantities are the moments of the solute distribution in the filament about the moving centroid of the solute mass. The effective dispersion coefficient can be calculated from the long time behavior of the variance of the solute distribution. Aris's expression for the effective dispersion coefficient in the long time limit is :

(2.16)
$$D_{eff}^* = \frac{1}{2} \lim_{t \to \infty} \frac{d\sigma^{*2}}{dt} = D^* + M \frac{w_0^2 \overline{u}^{*2}}{D^*}.$$

In the above equation, w_0 is a characteristic width of the channel, D is the molecular diffusivity and \overline{u}^* is the mean flow rate. All quantities indicated by asterisks are dimensional. M is a numerical prefactor which depends on the shape of the channel cross-section. For example, for circular cross-sections $M = \frac{1}{48}$. The Method of Moments has been used to study dispersion in subjects as diverse as porous media and transport of silts in rivers and estuaries in addition to dispersion in microfluidic systems, see [62] for a broad overview. Other methods, by with which Equation (2.16) has been derived include multiple scale asymptotics (Fife and Nicholes [63]), a mean and fluctuation method [64] inspired by turbulent transport models [65] and the dynamic theory of center manifolds [66, 67]. Taylor-Aris dispersion with inert walls is also known as shear-induced dispersion, as it is caused by nonuniform or sheared flow.

2.10. Taylor-Aris Dispersion with Active Walls

Traditionally, in the literature, dispersion under an irreversible loss to the wall and dispersion under a reversible adsorption processes have been treated in separate contexts. In this section, we will resort to classify wall interactions accordingly, although one purpose of this work is to treat slow/fast, reversible/irreversible interactions under the same theoretical framework.

2.10.1. Dispersion with Irreversible Wall Loss

Sankarasubramanian and Gill [68] and Lungu and Moffatt [69] developed approaches to treat advection-diffusion equations for a scalar c with a process causing a linear irreversible loss on the wall of the form:

(2.17)
$$(D\nabla c \cdot \hat{\mathbf{n}} + \beta^* c) \mid_w = 0$$

where $\hat{\mathbf{n}}$ is the wall normal and β^* characterizes the speed of the irreversible wall loss. The symbol $|_w$ indicate evaluation of the bracketed quantity on the wall. Sankarasubramanian and Gill [68] used an expansion in the area averaged concentration \overline{c} and its axial derivatives to represent the concentration field; Lungu and Moffatt used Fourier transforms and longwave approximation of the resultant eigen-value problems to arrive at effective dispersion coefficients of the following form:

(2.18)
$$D_{eff}^* = D^* + M\left(\frac{\beta w_0}{D^*}\right) \frac{w_0^2 \overline{u}^{*2}}{D^*}$$

where M, unlike in Equation (2.16) depends on the wall loss coefficient β^* . Sankarasubramanian and Gill concluded that in the presence of the irreversible wall loss, the center of mass of the distribution of solute particles travel faster than the mean speed of flow. This is because slow-moving solute particles near the wall are selectively removed by the adsorption process whereas the faster particles near the centerline remain unaffected. However, their analysis was restricted to circular cylinders. Lungu and Moffatt's analysis [69] can handle arbitrary cross-sections but cannot resolve the above-mentioned effect on the center of mass motion in its leading order long wave solution. However, they have outlined the method of incorporating higher harmonics in their paper.

2.10.2. Dispersion with Reversible Adsorption-Desorption on Walls

In separations based on the chromatographic principle, the characteristic time scale of both adsorption and desorption of the solute is much shorter than the migration time of the solute in the separation device. The total mass of solute in the stationary phase bears a constant ratio to that in the mobile phase under this condition, this ratio is known as partition coefficient [25]. The dynamics of migration and band broadening in chromatography can be predicted from stochastic considerations [29] as well as from the continuum-based mass transfer [70, 28]. We will briefly examine the common features of continuum-based approaches in the literature, because of their relevance to our work. The Method of Moments [70] and an approach based on small departures from equilibrium between adsorption and desorption [28] were first used to obtain expressions for the effective dispersion coefficient in terms of the partition coefficient K' of the form:

(2.19)
$$D_{eff}^* = D^* + M(K')\frac{w_0^2\overline{u}^{*2}}{D^*} + N(K')\frac{\overline{u}^{*2}}{k_d}$$

In the last term, k_d is the desorption rate constant of the wall interaction. The role of the last term was resolved by the analysis of Aris [70], but not that of Golay [28]; it has a significant contribution under conditions when the adsorption-desorption is fast, but not infinitely fast. The speed of the center of mass is slowed down by a factor 1 + K'. The theory by Aris [70] was derived for arbitrary cross-sectional shape.

2.11. Dispersion in Axially variable Flows With Wall Interactions

The theory of center manifolds was applied by Mercer and Roberts [67] to calculate dispersion of an inert solute in the axially varying gap between parallel plates. A multiple scale asymptotic method was applied by Bryden and Brenner [71] to study dispersion in cones. In these problems the variation in the flow field is a direct consequence of the axial variations in the channel geometry. In light of the fact that geometries other than cone or plane channel are common in microfluidic applications, we would calculate the dispersion of solutes in straight capillaries of an arbitrary axially varying cross-sectional shape in this work. The flow variations may or may not arise from geometrical effects, as in the above two studies. For example, the electroosmotic flow used in microfluidic separations is frequently rendered axially variable due to the presence of wall inhomogeneities affecting the zeta potential. We will also treat the effect of solute adsorption-desorption, since this effect is significant in a microfluidic channel as a consequence of its large surface to volume ratio. Despite this importance of axial variations and wall interactions in microfluidic separations, no previous work to the author's knowledge deals with predicting dispersion in the presence of adsorptiondesorption as well as axial variability of the flow.

The continuum-based description of mass transfer with adsorption-desorption on the walls will be solved in this work with a multiple scale asymptotic method that is substantially similar to [63] and is based on the foundations laid in [31]. This method can predict the three-dimensional distribution of the solute concentration unlike the Method of Moments. Axially variable cross-sections and flows will be treated in this work with the specification of an arbitrary kinetic function (not necessarily linear) on the wall. Fast linear adsorption characteristic of chromatographic interactions will be treated in this work as a special case of a more general problem of adsorption with arbitrary kinetics. Numerical comparisons will be made to test the asymptotic predictions. This work will also circumvent the need for costly numerical solution of partial differential equations in several spatial variables [72], as the asymptotic approach effectively identifies slow manifolds on which the dynamics is projected[67].

2.12. Summary

We have provided background material on electroosmotic flow and dispersion in presence and absence of adsorption-desorption in this chapter, while surveying the literature relevant to this work. The next three chapters will constitute the core of this thesis and will deal with electroosmotic flow, dispersion in axially invariant and in axially variable problems.

CHAPTER 3

Electroosmotic Flow in a Rectangular Channel under Axially Variable Zeta Potential

3.1. Background

When the characteristic length scale in an electroosmotic flow (EOF) problem is much larger than the Debye length scale, the flow field outside the Debye layer can be obtained by solving the Navier Stokes Equations with Helmholtz-Smoluchowski (HS) slip boundary condition on the liquid-solid interface. The HS boundary condition requires the specification of the zeta potential (ζ) at the liquid-solid interface, which characterizes the potential change within the Debye Layer. In this chapter, we will study the fluid flow in a rectangular channel (Figure 3.1) under axially variable zeta potentials in the thin Debye Layer limits. This translates to having an axially variable Helmholtz-Smoluchowski (HS) slip boundary condition on the walls of the rectangular channel. The electroosmotic flow in the channel will be solved numerically for several representative problems with variable zeta potential on the walls and the results will be used to test the predictions of available approximate analytical theory.

3.1.1. Governing Equations

Figure 3.1 shows the rectangular channel. The width is 2b and height is 2c. The x-axis is along the longitudinal axis of the capillary. The length of the capillary is L. The zeta potentials on the walls AB, BC, CD and DA are $\zeta_{AB}(x)$, $\zeta_{BC}(x)$, $\zeta_{CD}(x)$ and $\zeta_{DA}(x)$ respectively; these parameters could vary with x but not with y or z. The flow velocity components in x, y and z directions are u, v and w, respectively. For the rectangular channel shown in Figure 3.1 subject to a constant electric field E_0 along its length (in the x-direction), the equations governing the electroosmotic flow field at steady state, assuming incompressible flow become:

(3.1)
$$\rho \nabla \cdot \mathbf{u} \mathbf{u} = -\nabla p + \mu \nabla^2 \mathbf{u}$$

$$(3.2) \nabla \cdot \mathbf{u} = 0$$

$$(3.3) \begin{aligned} u(x,y,z=c) &= -\frac{\kappa E_0 \zeta_{BC}}{4\pi\mu}; & v(x,y,z=c) = 0; & w(x,y,z=c) = 0 \\ u(x,y,z=-c) &= -\frac{\kappa E_0 \zeta_{DA}}{4\pi\mu}; & v(x,y,z=-c) = 0; & w(x,y,z=-c) = 0 \\ u(x,y=b,z) &= -\frac{\kappa E_0 \zeta_{AB}}{4\pi\mu}; & v(x,y=b,z) = 0; & w(x,y=b,z) = 0 \\ u(x,y=-b,z) &= -\frac{\kappa E_0 \zeta_{CD}}{4\pi\mu}; & v(x,y=-b,z) = 0; & w(x,y=-b,z) = 0. \end{aligned}$$

Using ζ_0 as a characteristic scale for zeta potential, a characteristic scale $u_e = -\frac{\kappa E_0 \zeta_0}{4\pi \mu}$ for velocity components u, v, w can be constructed. The width (2b) of the channel in the y direction will be used to scale distances in all coordinate directions and the pressure will be scaled by $(\mu u_e/2b)$. Normalized with this scales the above equations become:

(3.4)
$$Re\nabla \cdot \mathbf{u}^* \mathbf{u}^* = -\nabla p^* + \nabla^2 \mathbf{u}^*$$

$$(3.5) \nabla \cdot \mathbf{u}^* = 0$$



Figure 3.1: Geometry of the rectangular channel showing a typical cross-section ABCD. The side AB is at y = -b, CD is at y = b, BC is at z = +c and DA is at z = -c. The entrance and exit cross-sectional planes are at x = 0 and x = L, respectively.

$$\begin{aligned} & (3.0) \\ & u^*(x^*, y^*, z^* = c/2b) = \zeta^*_{BC}; \quad v^*(x^*, y^*, z^* = c/2b) = 0; \quad w^*(x^*, y^*, z^* = c/2b) = 0 \\ & u^*(x, y, z^* = -c/2b) = \zeta^*_{DA}; \quad v^*(x^*, y^*, z^* = -c/2b) = 0; \quad w^*(x^*, y^*, z^* = -c/2b) = 0 \\ & u^*(x, y = 0.5, z) = \zeta^*_{AB}; \quad v^*(x, y = 0.5, z) = 0; \quad w^*(x, y = 0.5, z) = 0 \\ & u^*(x, y = -0.5, z) = \zeta^*_{CD}; \quad v^*(x, y = -0.5, z) = 0; \quad w^*(x, y = -0.5, z) = 0. \end{aligned}$$

The numerical calculation involved solving the above equations for u^*, v^*, p^* with prescribed zeta potentials ζ^* on the walls and Reynolds number, Re and the aspect ratio c/b as the parameters. Here onwards, the asterisks will be dropped and all quantities mentioned in the text will be non-dimensionalized according to the scales in this section, unless mentioned otherwise.

3.1.2. Analytical results from Lubrication Theory

(2 c)

An analytical treatment of the electroosmotic flow (EOF) problem (in the limit of infinitely thin Debye layers) where the characteristic length scale of the zeta potential variation on the walls is much larger than a characteristic linear dimension of the channel cross-section can be made using lubrication theory [15]. Lubrication theory is an asymptotic approach often employed in solving fluids problems where the fluid flows through a gap but the gap width is 'slowly varying'; that is, it does not change much over distances of the order of the gap width itself. The name 'lubrication theory' derives from one of the earliest applications of the theory to the flow of oil or other lubricant in the narrow gap between an axle and the shaft in which it rotates or between other moving parts in machinery [49]. The variation of the gap between two surfaces sliding against each other leads to the appearance of a local pressure distribution to preserve the same volume flow rate through each cross-section, even if no pressure difference is externally imposed. Similarly, in case of an EOF, the variation in zeta potential on the wall leads to the appearance of a local pressure distribution to preserve the same volume flow rate through each cross-section.

The solution process in [15] deals with the general situation of (a) variable channel crosssection and (b) variable zeta potential, with the assumption that the smallest axial scale Lfor the variation (of cross-section or zeta potential) is much larger than a typical linear dimension of the cross-section w_0 . Thus, $\epsilon = w_0/L$ can be used as a small parameter for expressing the velocity components (u, v and w), the pressure (p) and the electric potential (ϕ) as an asymptotic series of increasing powers of ϵ . The Navier Stokes equations for fluid flow (subject to HS slip conditions in the limit of infinitely thin Debye layers) and the Gauss Law for electric potential (with no volumetric charge density in the limit of infinitely thin Debye layers) is nondimensionalized in [15] with scales consistent with the lubrication approximation (the distances in axial directions are measured in units of L, in other directions the unit of length is w_0).

The current problem (encompassing the test cases A-D in Section 3.2) is a special case of the general situation addressed in [15], because we can assume that (a) cross-section is constant (b) externally applied pressure difference across the channel is zero and (c) the zeta potential varies only along the axial (x) direction while being piece-wise constant in y and z. Assuming the above simplifies the problem considerably (e.g. it is no longer necessary to solve the electric potential distribution through asymptotic approximation). Some important characteristics of the leading order fluid flow problem (Equations (3.15)-(3.19) in [15]) under the lubrication approximation are stated below.

- (i) the axial velocity u is of order one if measured in units of u_e and the components of velocity in the plane of the cross-section (v and w) are of order ε, if measured in units of u_e.
- (ii) the pressure measured in the Stokesian scale $\mu u_e/w_0$ is of order $1/\epsilon$, so that the pressure gradients in the y and z directions (y and z co-ordinates are measured in units of $w_0 = 2b$) have to be zero to the leading order to obey the v and w momentum equations. The axial pressure gradient is non-zero in general and is of order one.
- (iii) inertia and axial diffusion is negligible in the u momentum equation, the leading order balance is between the u-momentum diffusion in the cross-sectional directions and the axial pressure gradient.

In the remainder of this section, the main steps in the lubrication theory are described after [15] in terms of dimensional variables. Please note in this context that there are some typographic errors in that reference¹. The solution to the leading order axial velocity field can be written as a pressure-driven ("locally Poiseuille") part and a "pure EOF" as follows:

(3.7)
$$u = -\frac{u_p}{\mu}\frac{dp}{dx} + \frac{\kappa E_0\psi}{4\pi\mu}.$$

Equation (3.7) is a solution of the leading order approximation to the u momentum equation and the corresponding boundary conditions only if u_p and ψ satisfy Equation (3.8)

¹Corrigenda to [15]: (1) the exponent of $(2/\pi)$ in Equation (4.34) should be 5. (2) the denominator on the left hand side of Equation (4.61) should read 2n + 1. (3) in Equation (4.62) the number 16 should be replaced by 8 and the distribution of zeta potential should be $\zeta_h^+ = \zeta_1$ and ζ_0 on the other sides.

and (3.9) for the cross-section in Figure 3.1:

$$\nabla^2 u_p = -1$$

$$u_p(z = \pm c) = 0$$

$$(3.8)$$

$$u_p(y = \pm b) = 0$$

and

$$\nabla^2 \psi = 0$$

$$\psi(z=c) = -\zeta_{BC}$$

$$\psi(z=-c) = -\zeta_{DA}$$

$$\psi(y=-b) = -\zeta_{AB}$$

$$\psi(y=b) = -\zeta_{CD}.$$

The quantity $u_p(y, z)$ is numerically the same as the velocity distribution in a fullydeveloped flow of a fluid of unit viscosity in a rectangular channel driven solely by a unit pressure gradient. It has dimensions of length squared. The first term in the right hand side of Equation (3.7), $\frac{u_p}{\mu} \frac{dp}{dx}$ fails to satisfy the HS slip boundary conditions by itself. The second term containing the function ψ is required to satisfy the HS slip boundary conditions. The fact that the mean flow (\bar{u}) has to be axially invariant to preserve the continuity of the fluid in a channel of constant cross-section leads to an expression for the $\frac{dp}{dx}$ distribution. Averaging Equation (3.7) over the cross-section leads to:

(3.10)
$$\bar{u} = -\frac{\overline{u}_p}{\mu}\frac{dp}{dx} + \frac{\kappa E_0\psi}{4\pi\mu}.$$

Since applied external pressure drop $p_{entrance} - p_{exit} = 0$, the above equation averaged over the axial co-ordinate x gives:

(3.11)
$$\bar{u} = \frac{\kappa \langle \psi \rangle}{4\pi\mu} E_0$$

where $\langle \rangle$ indicates average in the axial direction, that is, $\langle \cdots \rangle = L^{-1} \int_0^L (\cdots) dx$. Using Equation (3.10) in Equation (3.11):

(3.12)
$$\frac{dp}{dx} = \frac{\mu u_e}{\bar{u}_p} \frac{(\langle \overline{\psi} \rangle - \bar{\psi})}{\zeta_0}.$$

Using Equation (3.12) in Equation (3.7) we get:

(3.13)
$$\frac{u}{u_e} = -\frac{u_p}{\bar{u}_p} \frac{\left(\langle \overline{\psi} \rangle - \bar{\psi}\right)}{\zeta_0} - \frac{\psi}{\zeta_0}$$

The above Equation will be referred to as the 'theoretical u/u_e ' for comparison with numerical results in Section 3.4.1 with ψ , $\bar{\psi}$, u_p and $\bar{u_p}$ calculated as follows.

For channels with identical $\zeta(x)$ distribution on its walls, $\psi = \zeta(x)$ is a solution to Equation (3.9). Therefore, $\overline{\psi} = \zeta(x)$ and $\langle \overline{\psi} \rangle = \langle \zeta \rangle$. When $\zeta(x)$ is not identical on the four walls (as in Figure 3.1), the ψ distribution can be obtained by solving Equation (3.9) using separation of variables, superposition and symmetry principles:

(3.14)
$$\psi(y, z, \zeta(x)) = f(y, z, b, c, \zeta_{AB}(x)) + f(z, -y, c, b, \zeta_{BC}(x)) + f(-y, z, b, c, \zeta_{CD}(x)) + f(z, y, c, b, \zeta_{DA}(x)).$$

Here, $f(y, z, b, c, \zeta(x))$ is the ψ distribution in Figure 3.1 if the wall AB at y = -b has $\psi = -\zeta$ and all other walls have $\psi = 0$:

(3.15)
$$f(y,z,b,c,\zeta(x)) = \sum_{n=1}^{\infty} \tilde{\zeta}(x,n) \; \frac{\sinh\left[\frac{n\pi}{2b}(y-b)\right]}{\sinh\frac{n\pi c}{b}} \sin\left[\frac{n\pi}{2b}(z+c)\right].$$

Here, the coefficient $\tilde{\zeta}(x,n)$ is the sine transform of the $\zeta(x)$ on each edge defined by:

(3.16)
$$\tilde{\zeta} = 1/L \int_{-\alpha}^{\alpha} \zeta \sin\left[\frac{n\pi}{2\alpha}(\eta + \alpha)\right] d\eta$$

where $\alpha = b$ for edges *BC* and *DA* and $\alpha = c$ for edges *AB* and *CD* in Figure 3.1. In case of a purely axial distribution of zeta potential, $\zeta = \zeta(x)$, the above integral for any edge evaluates to the same functional form:

(3.17)
$$\tilde{\zeta}(x,n) = \frac{2\left[1 - (-1)^n\right]}{n\pi} \zeta(x).$$

The expressions for $\bar{\psi}(x)$ calculated by averaging Equation (3.14) is:

(3.18)
$$\bar{\psi} = -\frac{\zeta_{AB}(x) + \zeta_{CD}(x)}{2} + \frac{b}{c} \left[\zeta_{AB}(x) + \zeta_{CD}(x) - \zeta_{BC}(x) - \zeta_{DA}(x) \right] S_3(b,c)$$

where the quantity S_3 is defined as:

(3.19)
$$S_3(b,c) = \left(\frac{2}{\pi}\right)^3 \sum_{n=0}^{\infty} \frac{1}{(2n+1)^3} \tanh\left[(2n+1)(\pi c/2b)\right].$$

The $u_p(y, z)$ distribution obtained by solving Equation (3.8) is :

$$u_p(y,z) = \frac{1}{2}b^2 - \frac{1}{2}y^2 - 2b^2\left(\frac{2}{\pi}\right)^3 \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n+1)^3} \frac{\cosh[(2n+1)(\pi z/2b)]}{\cosh[(2n+1)(\pi c/2b)]} \cos[(2n+1)(\pi y/2b)].$$

The expression for \bar{u}_p found by averaging the above equation is:

(3.21)
$$\bar{u}_p = \frac{b^2}{3} - 2\frac{b^3}{c}S_5(b,c)$$

where the quantity S_5 is defined as:

(3.22)
$$S_5(b,c) = \left(\frac{2}{\pi}\right)^5 \sum_{n=0}^{\infty} \frac{1}{(2n+1)^5} \tanh\left[(2n+1)(\pi c/2b)\right].$$

3.1.3. Analytical result for Stokes Flow between Parallel Plates

An analytical solution for Stokes flow between parallel plates subject to $\zeta^+ = \zeta^- = \zeta_0 + \Delta\zeta \cos(2\pi x/\lambda)$ is summarized here in the thin Debye layer limit after Ajdari [18]. This is relevant to the Case E discussed in Section 3.2. The problem of Stokes flow (Re = 0) between two parallel planes $(c/b \to 0)$ with arbitrary surface charge distribution has been solved by Ajdari [18] and Long, Stone and Ajdari [40]. The problem can be decomposed into the solution of the response to a single wavelength λ of charge modulation in two configurations : (a) $\sigma^+ = \sigma^- = \sigma \cos(2\pi x/\lambda)$ and (b) $\sigma^+ = -\sigma^- = \sigma \cos(2\pi x/\lambda)$. Here '+'and '-' denote the top and bottom walls at z = +c and z = -c respectively. The configuration (a) will be relevant to Case E discussed in Section 3.2, though the configuration (b) can be solved on similar lines.

The solution method presented in [18] involves solving the combined electrostatic and hydrodynamic equations in the low electrostatic potential (LEP) limit (or under Debye-Hückel approximation) and then taking the limit of thin Debye layers ($\lambda_D/c \rightarrow 0$ and $\lambda_D/\lambda \rightarrow$ 0). However, a direct derivation is also possible using the HS slip boundary conditions valid in the thin Debye layer (TDL) limit. The corresponding problem statement is:

(3.23)

$$\mu \nabla^2 \mathbf{v} = \nabla p$$

$$\nabla \cdot \mathbf{v} = 0$$

$$w(x, \pm c) = 0$$

$$u(x, \pm c) = -\frac{\kappa E_0 \Delta \zeta}{4\pi \mu} \cos\left(2\pi x/\lambda\right).$$

This problem can be reformulated in terms of the streamfunction Ψ defined such that $u = \frac{\partial \Psi}{\partial z}$ and $v = -\frac{\partial \Psi}{\partial x}$ as :

(3.24)

$$\nabla^{4}\Psi = 0$$

$$\Psi(x, \pm c) = 0$$

$$\frac{\partial\Psi(x, \pm c)}{\partial z} = -\frac{\kappa E_{0}\Delta\zeta}{4\pi\mu}\cos\left(2\pi x/\lambda\right).$$

Solving this problem by separation of variables and the linear superposition of the resultant streamfunction with the streamfunction for a uniform flow $u_e = -\frac{\kappa E_0 \zeta_0}{4\pi \mu}$ gives the following Ψ for Stokes flow between parallel plates subject to $\zeta^+ = \zeta^- = \zeta_0 + \Delta \zeta \cos(2\pi x/\lambda)$ in the thin Debye layer limit :

(3.25)
$$\Psi(x,z) = \frac{\kappa E_0 \zeta_0}{4\pi\mu} \left(z + \frac{\Delta\zeta}{\zeta_0} \cos\left(qx\right) f(z) \right)$$

(3.26)
$$f(z) = \frac{c \cosh(qc) \sinh(qz) - z \sinh(qc) \cosh(qz)}{qc - \sinh(qc) \cosh(qc)}$$

In the above equation, $q = 2\pi x/\lambda$. This analytical solution to the flow between parallel plates is expected to become relevant as (a) the aspect ratio of a rectangular channel is lowered progressively at constant wavelength λ , or (b) as $\lambda < 2b$ is lowered progressively at constant aspect ratio. The latter limit is explored at constant aspect ratio (c/b = 0.2) in the Case E mentioned in Section 3.2 and the results are presented in Section 3.4.2.

3.2. Test Problems for Numerical Simulation of Electroosmotic Flow with Variable Zeta Potential

The following cases will be studied numerically for comparison with available theory (here ζ_0 , ζ_1 , α , λ and $\Delta \zeta$ are given parameters). Other symbols used below have the same meaning as in Section 3.1.1 and Figure 3.1:

Case A:
$$\zeta_{AB} = \zeta_{CD} = \zeta_{DA} = \zeta_0, \ \zeta_{BC} = \zeta_1.$$

Case B: $\zeta_{AB} = \zeta_{CD} = \zeta_{DA} = \zeta_0, \ \zeta_{BC} = \zeta_0 [1 - \exp(-\alpha x)], \ c/b = 1.$
Case C: $\zeta_{AB} = \zeta_{CD} = \zeta_{DA} = \zeta_{BC} = \zeta_0 [1 - \exp(-\alpha x)], \ c/b = 1.$
Case D: $\zeta_{AB} = \zeta_{CD} = \zeta_{DA} = \zeta_0, \ \zeta_{BC} = \zeta_0 - \Delta\zeta \sin(2\pi x/\lambda), \ d < \lambda \le L, \ c/b = 0.5.$
Case E: $\zeta_{AB} = \zeta_{CD} = \zeta_{DA} = \zeta_{BC} = \zeta_0 + \Delta\zeta \cos(2\pi x/\lambda), \ c/b = 0.2.$

The configuration of Case A is motivated by the situation where an electrophoretic channel is made by bonding a cover slip on top of a channel etched on a substrate (see the left panel of Figure 3.2 for a schematic). Case B combines both features; the lack of equality of the zeta potential on all four walls as well as axial variations of ζ on one of the walls. The exponential model for the axial variation has been used by [50] to model an experimental situation where the reduction in the zeta potential in the axial direction is due to adsorption of contaminants from an solute plug [20] (see the right panel of Figure 3.2). Case C is similar to Case B except that the effect of axial variations alone is studied. The analytical solutions for Case C and Case B can be calculated on the basis of lubrication theory in [15]. The sinusoidal fluctuation studied in Case D is useful because in the Stokes flow limit (Re = 0) the flow problem is linear. Thus, any problem involving axial variation in zeta could be reduced to a sequence of problems involving sinusoidal variations. Furthermore the sine profile gives a qualitative idea of how the flow properties might depend upon the amplitude and length scale of any fluctuation in zeta. In Case E the wavelength of applied zeta potential is progressively decreased from $\lambda = L$ to values lower than 2b. For $\lambda/2b \leq 1$ in Case E, the lubrication theory is not expected to be applicable. However, if λ is small enough in relation to the gap between the side walls 2b, the theory of Stokes flow (Re = 0) between parallel plates [18] becomes relevant. The flow is driven by a constant electric field E_0 , and the Helmholtz-Smoluchowski slip velocity for $\zeta = \zeta_0$:

(3.27)
$$u_e = -\frac{\kappa \zeta_0 E_0}{4\pi\mu}.$$

will be taken as a reference velocity. The width 2b will be taken as the reference length. Then the dimensionless parameters in this problem are (a) the Reynolds number $\text{Re} = \rho u_e(2b)/\mu$ where ρ is the (constant) density of the fluid (b) the aspect ratio, (c/b) (c) the dimensionless channel length, L/(2b) (d) the parameter αL (e) the zeta potential ratio, ζ_1/ζ_0 (f) the dimensionless amplitude $\Delta \zeta/\zeta_0$ (g) the ratio λ/L . Of these, two of the parameters will be held fixed: Re = 1 and L/(2b) = 20 (except for wavelengths smaller than 2b in Case E, as discussed below). In microfluidic applications $\text{Re} \sim 1$, and further this scaling is implicit in the lubrication theory analysis we wish to check. For a 50 μ m wide channel that is 2 cm long, L/(2b) = 400. Thus, a choice of 20 is much smaller than what would be considered typical. However we chose this lower value so as not to make the computational time unduly long. Further, if the lubrication theory works well here, its performance would only get better with larger L/(2b).



(a) Microfluidic capillary with cover slip



(b) Zeta potential variation due to contamination by sample

Figure 3.2: Figure 3.2(a) shows schematically the cross-section of a microfluidic channel etched on a substrate with the substrate-buffer ζ potential equal to ζ_1 and covered by a glass cover slip with the glass-buffer zeta potential equal to ζ_2 . This represents a configuration corresponding to Case A. Figure 3.2(b) shows the model of zeta potential variation assumed for channel walls contaminated by sample from CE in Case B and Case C. In Case E, the grid resolution requirements (when $\lambda/2b \leq 1$) can make the solution in a long channel $(L/(2b) \sim 20)$ unduly expensive in terms of computational memory and time. Therefore, Case E is restricted to Stokes flow (Re = 0), which has the advantage of not having a 'development region' near the inlet section of the channel. If $\lambda/2b \leq 1$, a channel of short length, L = 2b will be considered, and periodic boundary condition will be applied between the entrance and exit planes. The actual physical channel may be constructed by joining a large number of these periodic units. If $\lambda/2b > 1$, L/(2b) = 20 will be used with periodic boundary conditions. An aspect ratio c/b = 0.2 was used.

The pressure difference between the entrance and exit planes is assumed zero for all cases, of course in Case E the periodic boundary condition automatically ensures that it is zero. One of the flow properties we are interested in is the electroosmotic mobility, μ_{eo} defined as $\bar{u} = \mu_{eo}E_0$ where \bar{u} is the volume flux per unit area (the average velocity). The mobility will always be quoted as a ratio μ_{eo}/μ_{eo}^{ref} where μ_{eo}^{ref} is a 'reference mobility' for a uniform channel with $\zeta = \zeta_0$. The dimensionless pressure gradient is defined as

(3.28)
$$\pi_* = -\frac{(2b)^2}{\mu u_e} \frac{d\bar{p}}{dx}.$$

Here, \bar{p} denotes the pressure averaged over the area of cross-section. All calculated results are presented in dimensionless form so that actual physical value of parameters (such as the value of ζ_0) is never needed and never used in this dissertation.

3.3. Numerical Methods

The incompressible steady state Navier Stokes Equations (Equations (3.4) and (3.5)) with Helmholtz-Smoluchowski slip boundary conditions (Equation (3.6)) were discretized using a finite volume method. The grid was of a staggered type (see Figure 3.3) : the control volume for discretizing the momentum equation in a given direction (e.g. control volume for the velocity component u shown in Figure 3.3) was offset in that direction from the control volume for discretizing the continuity equation (control volume for calculating the pressure p) by a distance equal to half-width of the control volume for p. Calculation of pressure from the discretized momentum and continuity equations was done using the SIMPLER algorithm (Semi Implicit Method for Pressure Linked Equations Revised). The discretized equations for velocity components and pressure were solved using line-by-line TDMA (Tridiagonal Matrix Algorithm) discussed in [73].

The grid size was $\Delta z/2b = \Delta y/2b = \Delta x/4b = 0.05$ in Cases A to D. In Case E, the grid size was $\Delta z/2b = \Delta y/2b = \Delta x/2b = 0.0067$ for $\lambda = (2b)/12$, $\Delta z/2b = \Delta y/2b = \Delta x/2b = 0.001$ for $\lambda = (2b)/3$ and $\Delta z/2b = \Delta y/2b = \Delta x/4b = 0.025$ for $\lambda = L/10$ and $\lambda = L$.

In Cases A-D the boundary conditions at the entrance and exit planes x = 0, L/2b of the channel involved the prescription of pressure following an approach similar to that described in [74]. The boundary grid arrangement is summarized in the bottom panes of Figure 3.3. The discretized pressure equations are solved from p_2 to p_{n-1} , the value of $p_1 = p_{entrance}$ and $p_n = p_{exit}$ being given. The point p_2 is the right neighbor of p_1 and p_{n-1} is the left neighbor of p_n (not shown in the bottom panes of Figure 3.3). Here, the subscript varies along the discretized x axis (the axial co-ordinate of the channel) and n is the number of pressure control volumes in x direction.

The discretized momentum equations were solved from u_1 to u_{n-1} . Since, v = w = 0on the entrance and exit planes, application of continuity equation gives $\frac{\partial u}{\partial x} = 0$ there. Therefore, the continuity equation takes the discretized forms $u_0 = u_1$ and $u_n = u_{n-1}$ on the control volumes centered on the entrance and the exit planes (shown with dashed outlines in the bottom panes of Figure 3.3). The 'ghost point' velocities u_0 and u_n are necessary for solving the momentum equations for u_1 and u_{n-1} . In Case E, as mentioned earlier, periodic boundary conditions were used for the velocity components and pressure.

3.4. Comparison of Numerical Simulations to Asymptotic Theory

The results presented in Section 3.4.1 will correspond to Cases A, B, C, D mentioned in Section 3.2. These results will include a comparison with several analytical results (Equations (3.7)-(3.21) in Section 3.1.2) from the lubrication theory [15]. Case E, the only case where $\lambda < 2b$ will be explored will be treated separately in Section 3.4.2. Comparison will be made with the flow field (Equation (3.25) in Section 3.1.2) from the theory of electroosmotic flow between parallel plates [18] in addition to the lubrication theory. The conclusions from the comparisons in Cases A-E will be summarized in Section 3.5.

3.4.1. Results for Slowly Varying Wall Zeta Potential: Comparison with Lubrication Theory

Figure 3.4 shows the electroosmotic mobility μ_{eo} normalized by the reference mobility μ_{eo}^{ref} for Case A. These quantities are defined in Section 3.2 and may be calculated using the formulas presented in Section 3. The monotonic increase of μ_{eo}/μ_{eo}^{ref} with ζ_1/ζ_0 is expected, since a higher zeta potential corresponds to higher slip velocities. The sensitivity of the flow to changes in ζ_1/ζ_0 depends on the aspect ratio c/b, decreasing with increasing values of c/b. This is because when c/b is large, the face with the different ζ potential, $\zeta = \zeta_1$ is further removed from the bulk of the solution and consequently has a smaller effect on the overall fluid flux. The numerical results agree very well with the theory. This is to be expected, since when there are no axial variations at all, the asymptotic solution based on 'slow' axial variations become exact.



Figure 3.3: On the top left panel, the control volume for pressure (p) is shown shaded and its center is marked P; the symbols N, S, E, W are locations of northern, southern, eastern and western neighbors of the point P. On the top right panel, the control volume for the velocity component u is shown shaded. The symbols n, s, e, w denote northern, southern, eastern and western faces of the control volume with center at P on either panels. Control volumes for u momentum equation (solid outline) and continuity equation (dashed outline) near the entrance plane and exit plane projected on a constant z plane are shown on the bottom left and bottom right panels.

The dimensionless form of the negative pressure gradient π_* , (defined by Equation (3.28)) is shown in Figure 3.5 for Case B. The π_* calculated from the asymptotic theory using Equation (3.12) is also in good overall agreement. Figure 3.6 shows the corresponding mobility data μ_{eo}/μ_{eo}^{ref} both for Case B as well as Case C as a function of the dimensionless parameter αL . The asymptotic theory is expected to be accurate until about $\alpha \sim 1/(2b)$, that is, for $\alpha L \sim (L/2b) \simeq 20$ and this is consistent with curve 'b' (Case C) in Figure 3.6. In curve 'b'(Case B), the asymptotically theory is marginally more accurate as the boundary conditions in Case B (zeta potential variation on only one wall) is perturbed to a lesser degree than in Case C (zeta potential variation on all four walls.)

Figures 3.7 and 3.8 show the normalized pressure gradient, π_* , for the long ($\lambda = L$) and short ($\lambda = L/10$) wavelength cases of Case D with $\Delta \zeta/\zeta_0 = 0.5$. The short wavelength case corresponds to $\lambda = L/10 = 4b$, so that the lubrication approximation is only marginally satisfied. In both cases however the induced pressure gradient is very accurately predicted.

Figure 3.9 and Figure 3.10 show the contours of the numerically calculated $u(y, z)/u_e$ on the left panels (1a, 2a) and the contours calculated using lubrication theory on the right panels (1b, 2b) on the planes x/2b = 3.3 and x = 8.9. The same lines of constant u/u_e have been used for the theoretical and numerical result on a given plane. The two distributions are visually indistinguishable for $\lambda = L = 40b$ (Figure 3.9). The theoretical and the numerical u/u_e distributions with a smaller wavelength $\lambda = L/10 = 4b$ are of comparable accuracy in Figure 3.10, except for slight discrepancies. For example, in the region below the $u/u_e = 1$ isoline in (Figure 3.9), the changes in u/u_e occurs slightly less steeply (both in y and z directions) in the numerical results than in the lubrication theory result. As explored in Case E, this behavior should be more prominent in case of wavelengths of zeta potential variation shorter than the channel width 2b, where a boundary layer forms on the wall z = +c/2b, outside of which, there is slow variation.

Figure 3.11 and 3.12 show the normalized velocity u/u_e (Panel A) on the y = 0 line of the cross-sections shown in Figure 3.1) at four different axial locations indicated by the symbols in Figures 3.7 and 3.8. In the long wavelength case, the agreement with the theory is excellent but in the short wavelength case, slight discrepancies –of the order of one percent – is seen.

Equation (3.7) of Section 3 could be easily inverted (noting that if p does not depend on y and z then $p = \bar{p}$) and written in the form:

(3.29)
$$u_p = \mu \left(\frac{\kappa E_0 \psi}{4\pi \mu} - u\right) \left(\frac{d\bar{p}}{dx}\right)^{-1}.$$

If Equations (3.14) and (3.15) are used to evaluate ψ and the computed numerical results are used for u and \bar{p} in Equation (3.29), then this quantity, which can be given the physical meaning of "pressure driven part of the flow per unit pressure gradient" is a useful quantity to compare with theory. Indeed, in the lubrication limit, u_p is expected to be independent of everything but the channel geometry and should be given by Equation (3.20). Panel B in Figures 3.11 and 3.12 compares u_p extracted from the data [Case D with $\Delta \zeta/\zeta_0 = 0.5$] in this way with Equation(3.20). In both cases there is collapse of the data onto the curve, though the agreement is much better in the long wavelength limit (Figure 3.11) compared to the short wavelength case (Figure 3.12). Since the smallness of $\lambda/(2b)$ is a measure of the accuracy of the lubrication approximation, this is consistent with expectations.

Figure 3.13 is the same as Panel B in Figures 3.11 and 3.12 except that we vary the amplitude of the sine wave in Case D while keeping the wavelength fixed at $\lambda = L/5 = 8b$.

The amplitude $\Delta \zeta/\zeta_0$ is varied from 0.25 to 4. The quantity u_p defined in Equation (3.29) is plotted as a function of z/(2b) for y = 0 at two axial locations: x/2b = 9.8, 10.3. The theoretical curve, Equation (3.20) is shown by the solid line. The collapse of the data onto the theoretical curve is very good, even though the amplitude $\Delta \zeta/\zeta_0$ is not small. This is to be expected, since the lubrication theory is based on long axial length scales not small fluctuations in ζ . The deviation from the lowest order asymptotic theory however does depend on the amplitude, and generally the error increases with the amplitude of the fluctuations. This is indeed what is seen in Figure 3.13.

It is easily verified from Equation (3.11) that for Case D, the fluctuating part of the zeta potential does not contribute to the volume flux of fluid. Thus, for Case D, we expect $\mu_{eo}/\mu_{eo}^{ref} = 1$. This was indeed observed in all cases run for Case D. Deviations from unity only appeared in the third or fourth decimal places and consequently could not be distinguished from numerical truncation errors.



Figure 3.4: Electroosmotic mobility for Case A as a function of ζ_1/ζ_0 for various aspect ratios c/b. The curves labeled 'a', 'b', 'c', 'd' and 'e' are obtained for aspect ratio c/b = 0.25, 0.5, 1, 2 and 4, respectively. The symbol 'o' denotes the numerically calculated result and the solid line denotes the corresponding result from asymptotic theory.



Figure 3.5: Dimensionless negative pressure gradient (π_*) as a function of x/2b for Case B. The curves labeled 'a', 'b' and 'c' are obtained for $\alpha L = 115.13, 23.03$ and 12.79, respectively. The symbol 'o' denotes the numerically calculated result and the solid line denotes the corresponding result from asymptotic theory.



Figure 3.6: Electroosmotic mobility for Case B, indicated as curve (a) and for Case C indicated as curve (b) as a function of αL . The symbol 'o' denotes the numerically calculated result and the solid line denotes the corresponding result from asymptotic theory.



Figure 3.7: Dimensionless negative pressure gradient (π_*) as a function of x/2b for Case D with $\lambda = L = 40b$, c/b = 0.5 and $\Delta \zeta/\zeta_0 = 0.5$. The dots indicate numerically calculated results and the solid line corresponds to the calculation based on asymptotic theory. The points marked $*, \Delta$, \diamond and \Box denote the streamwise locations x/2b = 3.3, 8.9, 11.1, 16.7 for which velocity profiles are indicated by the corresponding symbols in Figure 3.11.



Figure 3.8: Dimensionless negative pressure gradient (π_*) as a function of x/2b for Case D with $\lambda = L/10 = 4b$, c/b = 0.5 and $\Delta \zeta/\zeta_0 = 0.5$. The dots indicate numerically calculated results and the solid line corresponds to the calculation based on asymptotic theory. The points marked $*, \Delta$, \diamond and \Box denote the streamwise locations x/2b = 3.3, 8.9, 11.1, 16.7 for which velocity profiles are indicated by the corresponding symbols in Figure 3.12.



Figure 3.9: Panel 1a and 2a show the contours of streamwise velocity $u(y, z)/u_e$ for Case D with $\lambda = L = 40b$, c/b = 0.5 and $\Delta \zeta/\zeta_0 = 0.5$ at the streamwise locations x/2b = 3.3 and x = 8.9 as a function of z/(2b). Panel 1b and 2b show the corresponding theoretically predicted distributions.



Figure 3.10: Same as Figure 3.9, except for $\lambda = L/10 = 4b$.


Figure 3.11: Panel A shows the streamwise velocity profiles $u(y = 0, z)/u_e$ for Case D with $\lambda = L = 40b, c/b = 0.5$ and $\Delta \zeta/\zeta_0 = 0.5$ as a function of z/(2b). Panel B shows the corresponding $u_p(y = 0, z)/(2b)^2$. The symbols: $*, \Delta, \diamond$ and \Box , denote numerically calculated profiles at the streamwise locations indicated in Figure 3.7. The solid line represents the corresponding profiles obtained from asymptotic theory.



Figure 3.12: Panel A shows the streamwise velocity profiles u(y = 0, z) for Case D with $\lambda = L/10 = 4b, c/b = 0.5$ and $\Delta \zeta/\zeta_0 = 0.5$ as a function of z/(2b). Panel B shows the corresponding $u_p(y = 0, z)/(2b)^2$. The symbols: $*, \Delta, \diamond$ and \Box denote numerically calculated profiles at the streamwise locations indicated in Figure 3.8. The solid line represents the corresponding profiles obtained from asymptotic theory.



Figure 3.13: $u_p(0,z)/(2b)^2$ on the planes x/2b = 9.8 and x/2b = 10.3 for two different values of $\Delta \zeta/\zeta_0$ with $\lambda = L/5 = 8b$ and c/b = 0.5 in Case D. The hollow and solid symbol of a given shape corresponds to $\Delta \zeta/\zeta_0 = 0.25$ and $\Delta \zeta/\zeta_0 = 4$, respectively. The round symbol corresponds to $u_p(0,z)$ on the plane x/2b = 9.8 and the triangular symbol corresponds to $u_p(0,z)$ on the plane x/2b = 9.8 and the triangular symbol corresponds to $u_p(0,z)$ on the plane x/2b = 10.3.

3.4.2. Transition from Slow to Fast Variation in Wall Zeta Potential

As mentioned in the Section 3.2, Case E will be used to carry the lubrication theory beyond its zone of expected validity. For $\lambda < 2b$, and c < b comparisons with parallel plate theory [18] become relevant.

In Figures 3.14-3.18 the symbols indicate the computed velocity profiles for Case E at several axial locations for $\lambda/(2b) = 20$, $\lambda/(2b) = 2$ and 1/3 and 1/12. Figures 3.14 and 3.15 pertain to wavelength larger than the channel width 2b and have been generated from a simulation using a channel of length L/2b = 20, while the remaining are from a simulation using L/2b = 1 as discussed in Section 3.2. In Panel A of these figures the computed solution is compared with the lubrication theory result, Equation (3.20). Expectedly, for $\lambda/(2b) = 20$ (or $\lambda/L = 1$), there is a good agreement between lubrication theory and the numerical result. However, the accuracy of the lubrication solution rapidly deteriorates with decreasing values of $\lambda/(2b)$. In particular, when $\lambda/(2b) = 1/12$ the lubrication solution is not even qualitatively correct.

For sufficiently short wavelength of oscillations in the ζ potential, the velocity perturbation is confined to a narrow region next to the wall [18]. Since in the short wavelength case one would expect that the presence of the side walls at $y = \pm b$ would be irrelevant, one might expect that $b \to \infty$ might be a more useful approximation than the lubrication limit in describing this situation. Fortunately, an exact analytical solution is known for Stokes flow between parallel plates in the infinitely thin EDL limit [18] (see Equation (3.25) in Section 3).



Figure 3.14: Panel A shows the streamwise velocity profiles u(y = 0, z) for Case E with $\lambda = L = 40b$, c/b = 0.2 and $\Delta \zeta/\zeta_0 = 0.1$ as a function of z/(2b) compared with the theoretical values calculated using Equation (3.7). Panel B shows u(y = 0, z) calculated by Equation (3.25) based on the theory presented by Ajdari [18]. The symbols: $*, \Delta, \diamond$ and \Box denote numerically calculated profiles at the streamwise locations x/2b = 2, 4, 12, 14. The solid line represents the corresponding profiles obtained from the relevant theory.



Figure 3.15: Panel A shows the streamwise velocity profiles u(y = 0, z) for Case E with $\lambda = L/10 = 4b$, c/b = 0.2 and $\Delta \zeta/\zeta_0 = 0.1$ as a function of z/(2b) compared with the theoretical values calculated using Equation (3.7). Panel B shows u(y = 0, z) calculated by Equation (3.25) based on the theory presented by Ajdari [18]. The symbols: $*, \Delta, \diamond$ and \Box denote numerically calculated profiles at the streamwise locations x/2b = 2.3, 4.9, 12.6, 14.4. The solid line represents the corresponding profiles obtained from the relevant theory.



Figure 3.16: Panel A shows the streamwise velocity profiles $u(y = 0, z)/u_e$ for Case E with $\lambda/(2b) = 1$, c/b = 0.2 and $\Delta \zeta/\zeta_0 = 0.1$ as a function of z/(2b) compared with the theoretical values calculated using Equation (3.7). Panel B shows $u(y = 0, z)/u_e$ calculated by Equation (3.25) based on the theory presented by Ajdari [18]. The symbols: $*, \Delta, \Diamond$ and \Box denote numerically calculated profiles at the streamwise locations x/2b = 0.1, 0.2, 0.6, 0.7. The solid line represents the corresponding profiles obtained from the relevant theory.



Figure 3.17: Same as Figure 3.16, except that $\lambda/(2b) = 1/3$.



Figure 3.18: Same as Figure 3.16, except that $\lambda/(2b) = 1/12$.

In Panel B of Figures 3.14-3.18 the computed solution is compared with the $u(y = 0, z)/u_e$ obtained from Ajdari's parallel plate theory using Equation (3.25). It is seen that for $\lambda/(2b) = 1$, the computed solution agrees better with Ajdari's parallel plate solution than the lubrication theory of Section 3. Further, as $\lambda/(2b)$ is further reduced, the agreement with lubrication theory gets progressively worse while the agreement with Ajdari's solution gets progressively better. This is exactly the behavior one would expect, since the two theories are complementary in the sense that their respective zones of asymptotic convergence are $\lambda \gg (2b)$ (lubrication theory) and $\lambda \ll (2b)$ (Ajdari's solution). It should be noted, however, the two-dimensionality of the flow field required for the parallel plate approximation is invalid in a region near the side-walls whose thickness is of the order of the wavelength.

3.5. Summary

In this chapter, the inhomogeneous electroosmotic flow field in rectangular channels under variable wall zeta potential were solved for several test problems (Cases A-E) inspired by microfluidic applications through direct numerical simulation as well as analytical approximations. It was observed that the lubrication theory developed in [15], when specialized to rectangular channels under variable wall zeta potential, accurately represents the electroosmotic mobility, flow and pressure gradient distributions in case of asymmetric wall zeta potential (Case A) and zeta potential variations characteristic of solute adsorption being present on walls of a CE channel (Cases B and C). Cases D and E were designed to test the slow variation assumption in lubrication theory. The results from Case D showed that the lubrication theory can be used reliably for wavelengths considerably shorter than its theoretical limit of validity ($\lambda/L \rightarrow 0$), but not for wavelengths shorter than the channel width 2b (Case E). In case of Case E, a short-wavelength parallel-plate approximation based on the theory due to Ajdari [18] performs progressively better than the lubrication theory as the wavelength becomes progressively shorter than the channel width (2b).

CHAPTER 4

Dispersion in the Presence of Wall Interactions in the Absence of Axial Inhomogeneity

4.1. Theoretical Formulation

A charge-neutral species with volumetric concentration c is transported in a channel of arbitrary (but axially invariant) cross-section by the action of flow and molecular diffusion. The species is also adsorbed on the wall of the channel giving rise to a surface concentration s. We choose a co-ordinate system such that the x-axis coincides with the axis of the channel. The cross-section at a given axial location of the channel can be described by the region Ω in the y - z plane; its bounding curve being denoted by $\partial \Omega$. We will restrict ourselves in this chapter to flows that are steady, incompressible and axially invariant. The only nonzero velocity component u of such a flow is in the x direction and is independent of x.

In the subsequent discussion, a vector operator subscripted with Ω will denote the component of that operator in the plane of Ω , e.g. $\nabla_{\Omega} \equiv \frac{\partial}{\partial y} \hat{\mathbf{j}} + \frac{\partial}{\partial z} \hat{\mathbf{k}}$. Also, a bar over a quantity will denote an average defined at each axial location x and time t: for quantities defined within the channel (e.g. c and u) the average is over the two dimensional region Ω , for quantities defined on the wall of the channel (e.g. s) the average is over the one dimensional bounding curve $\partial\Omega$.

The flow field can be represented by $u = \overline{u} F(y, z)$ where \overline{u} is the average velocity over the cross-section and $\overline{F} = 1$. Choosing a characteristic dimension w_0 as the unit of length, w_0/u_e as the unit of time (where u_e is a velocity scale), c_0 as the unit of volumetric concentration and

 $w_0 c_0$ as the unit of surface concentration, the equations governing transport and adsorption can be written in terms of the non-dimensional parameter $\text{Pe} = \frac{u_e w_0}{D}$ (Peclet number)

(4.1a)
$$\frac{\partial c}{\partial t} + \overline{u}F\frac{\partial c}{\partial x} = \mathrm{Pe}^{-1}\nabla^2 c$$

(4.1b)
$$-\operatorname{Pe}^{-1}\nabla c \cdot \hat{\mathbf{n}}\Big|_{\partial\Omega} = \frac{\partial s}{\partial t}.$$

Here, $\hat{\mathbf{n}}$ is the unit vector normal to the wall.

To study the long-time limit, when the axial spreading has caused the typical length scale along the x axis to become much larger than the channel width, introduce the co-ordinates $T = \epsilon t$ and $X = \epsilon x$ where $\epsilon \ll 1$. Using these co-ordinates in the above governing equation, we get:

(4.2a)
$$\epsilon \frac{\partial c}{\partial T} + \epsilon \overline{u} F \frac{\partial c}{\partial X} - \epsilon^2 \mathrm{Pe}^{-1} \frac{\partial^2 c}{\partial X^2} = \mathrm{Pe}^{-1} \nabla_{\Omega}^2 c$$

(4.2b)
$$-\operatorname{Pe}^{-1}\nabla_{\Omega}c \cdot \hat{\mathbf{n}}\big|_{\partial\Omega} = \epsilon \frac{\partial s}{\partial T}.$$

The variables c and s can be expanded in powers of ϵ :

(4.3a)
$$c = c^{(0)} + \epsilon c^{(1)} + \cdots$$

(4.3b)
$$s = s^{(0)} + \epsilon c^{(1)} + \cdots$$

and substituted in Equations (4.2a) and (4.2b). Equating coefficients of like powers of ϵ we get a succession of problems, which we consider next.

At O(1), we get:

(4.4a)
$$\operatorname{Pe}^{-1} \nabla_{\Omega}^{2} c^{(0)} = 0$$

(4.4b)
$$-\operatorname{Pe}^{-1}\nabla_{\Omega}c^{(0)}\cdot\hat{\mathbf{n}}\big|_{\partial\Omega}=0.$$

Equations (4.4a) and (4.4b) imply $c^{(0)}$ is independent of the cross-sectional co-ordinates y, z. Thus, $c^{(0)}(X,T) = \overline{c}^{(0)}(X,T)$. This result will be used in subsequent equations.

At $O(\epsilon)$:

(4.5a)
$$\operatorname{Pe}^{-1}\nabla_{\Omega}^{2}c^{(1)} = \frac{\partial\overline{c}^{(0)}}{\partial T} + \overline{u}F\frac{\partial\overline{c}^{(0)}}{\partial X}$$

(4.5b)
$$-\operatorname{Pe}^{-1}\nabla_{\Omega}c^{(1)}\cdot\hat{\mathbf{n}}\big|_{\partial\Omega} = \frac{\partial s^{(0)}}{\partial T}.$$

To be able to solve Equation (4.5a) with the boundary condition given by Equation (4.5b), a solvability condition needs to be satisfied. This can be found by area averaging both sides of Equation (4.5a).

(4.6)
$$\frac{\partial \overline{c}^{(0)}}{\partial T} + \overline{u} \frac{\partial \overline{c}^{(0)}}{\partial X} = -\alpha \frac{\partial \overline{s}^{(0)}}{\partial T}.$$

In the above α is a geometrical parameter given by $\frac{\Gamma' w_0}{A'}$ where Γ' is the perimeter of the curve $\partial\Omega$ and A' is the area of the region Ω . In terms of dimensionless perimeter and area measured in units of w_0 and w_0^2 respectively, $\alpha = \frac{\Gamma}{A}$. Using Equation (4.6) in (4.5a):

(4.7a)
$$\operatorname{Pe}^{-1}\nabla_{\Omega}^{2}c^{(1)} = -\alpha \frac{\partial \overline{s}^{(0)}}{\partial T} + (F-1)\overline{u} \frac{\partial \overline{c}^{(0)}}{\partial X}$$

(4.7b)
$$-\operatorname{Pe}^{-1}\nabla_{\Omega}c^{(1)}\cdot\hat{\mathbf{n}}\big|_{\partial\Omega} = \frac{\partial s^{(0)}}{\partial T}.$$

Equation (4.7b) has solutions of the form :

(4.8)
$$c^{(1)} = \overline{c}^{(1)} + \operatorname{Pe}\left[-\alpha \frac{\partial \overline{s}^{(0)}}{\partial T} \Psi^{(0)}(y,z) + \overline{u}_0 \frac{\partial \overline{c}^{(0)}}{\partial X} \chi(y,z)\right]$$

where:

(4.9a)
$$\nabla_{\Omega}^{2}\Psi^{(0)} = 1$$

(4.9b)
$$\nabla_{\Omega}\Psi^{(0)} \cdot \hat{\mathbf{n}} = \frac{1}{\alpha} \frac{\partial s^{(0)}}{\partial t} / \frac{\partial \overline{s}^{(0)}}{\partial t}$$

$$\overline{\Psi^{(0)}} = 0.$$

and

(4.10a)
$$\nabla_{\Omega}^{2}\chi = F - 1$$

(4.10b)
$$\nabla_{\Omega}\chi\cdot\hat{\mathbf{n}}=0$$

(4.10c) $\overline{\chi} = 0.$

For use in equations to follow, we can define $\Psi = \Psi^{(0)} + O(\epsilon)$ such that:

(4.11a)
$$\nabla_{\Omega}^{2}\Psi = 1$$

(4.11b)
$$\nabla_{\Omega}\Psi\cdot\hat{\mathbf{n}} = \frac{1}{\alpha}\frac{\partial s}{\partial t}/\frac{\partial \overline{s}}{\partial t}$$

$$\overline{\Psi} = 0$$

where the right hand side of Equation (4.11b) is estimated to leading order accuracy.

Equation (4.10) suggests that χ is completely determined by the specification of crosssectional geometry and the flow profile $u/\overline{u} = F$. Equation (4.11) suggests that Ψ is completely determined by the specification of cross-sectional geometry and the wall reaction kinetics. However, in the majority of situations, Ψ will be determined solely by geometry, as discussed later in Section 4.3.

At $O(\epsilon^2)$:

(4.12a)
$$\operatorname{Pe}^{-1} \nabla_{\Omega}^{2} c_{2} = \frac{\partial c^{(1)}}{\partial T} + \overline{u} F \frac{\partial c^{(1)}}{\partial X} - \operatorname{Pe}^{-1} \frac{\partial^{2} \overline{c}^{(0)}}{\partial X^{2}}$$

(4.12b)
$$-\operatorname{Pe}^{-1}\nabla_{\Omega}c_{2}\cdot\hat{\mathbf{n}}\big|_{\partial\Omega} = \frac{\partial s^{(1)}}{\partial T}.$$

A solvability condition for Equation (4.12a) derived by averaging either sides of that equation and using Equation (4.12b) constrains $\bar{c}^{(1)}$ to obey :

(4.13)
$$\frac{\partial \overline{c}^{(1)}}{\partial T} + \overline{u} \ \overline{F \frac{\partial c^{(1)}}{\partial X}} - \operatorname{Pe}^{-1} \frac{\partial^2 \overline{c}^{(0)}}{\partial X^2} = -\alpha \frac{\partial \overline{s^{(1)}}}{\partial T}.$$

Using Equation (4.8) to evaluate the quantity with overbar in Equation (4.13):

$$\overline{F\frac{\partial c^{(1)}}{\partial X}} = \frac{\partial \overline{c}_1}{\partial X} + \operatorname{Pe}\left(-\alpha \overline{\Psi F}\frac{\partial^2 \overline{s}^{(0)}}{\partial X \partial T} + \overline{\chi F} \ \overline{u} \ \frac{\partial^2 \overline{c}^{(0)}}{\partial X^2}\right).$$

Inserting the last relationship in Equation (4.13):

(4.15)
$$\frac{\partial \overline{c}^{(1)}}{\partial T} + \overline{u} \frac{\partial \overline{c}^{(1)}}{\partial X} = \left[\operatorname{Pe}^{-1} - \operatorname{Pe} \overline{\chi F} \, \overline{u}^2 \right] \frac{\partial^2 \overline{c}^{(0)}}{\partial X^2} - \alpha \frac{\partial \overline{s}^{(1)}}{\partial T} + \alpha \operatorname{Pe} \overline{u} \, \overline{\Psi F} \, \frac{\partial^2 \overline{s}^{(0)}}{\partial X \partial T}.$$

Multiplying Equation (4.15) by ϵ and adding the result to Equation (4.6):

(4.16)
$$\frac{\partial \overline{c}}{\partial T} + \overline{u} \frac{\partial \overline{c}}{\partial X} = \epsilon \left(\operatorname{Pe}^{-1} - \operatorname{Pe} \overline{\chi F} \, \overline{u}^2 \right) \frac{\partial^2 \overline{c}^{(0)}}{\partial X^2} - \alpha \frac{\partial \overline{s}}{\partial T} + \epsilon \, \alpha \operatorname{Pe} \overline{u} \, \overline{\Psi F} \, \frac{\partial^2 \overline{s}^{(0)}}{\partial X \partial T} + O(\epsilon^2)$$

where $\bar{c} = \bar{c}^{(0)} + \epsilon \bar{c}^{(1)} + O(\epsilon^2)$ and $\bar{s} = \bar{s}^{(0)} + \epsilon \bar{s}^{(1)} + O(\epsilon^2)$. Adding the $O(\epsilon^2)$ terms $\epsilon^2 \alpha \operatorname{Pe} \bar{u} \frac{\partial^2 \bar{s}^{(0)}}{\partial X \partial T} \overline{\Psi} F$ and $\epsilon^2 \left(\operatorname{Pe}^{-1} - \operatorname{Pe} \overline{\chi} F \bar{u}^2 \right) \frac{\partial^2 \bar{c}^{(1)}}{\partial X^2}$ to above equations:

(4.17)
$$\frac{\partial \overline{c}}{\partial T} + \overline{u} \frac{\partial \overline{c}}{\partial X} = \epsilon \left(\operatorname{Pe}^{-1} - \operatorname{Pe} \overline{\chi F} \, \overline{u}^2 \right) \frac{\partial^2 \overline{c}}{\partial X^2} - \alpha \frac{\partial \overline{s}}{\partial T} + \epsilon \alpha \operatorname{Pe} \overline{u} \, \overline{\Psi F} \, \frac{\partial^2 \overline{s}}{\partial X \partial T} + O(\epsilon^2).$$

Reverting to original variables $t = T/\epsilon$ and $x = X/\epsilon$:

(4.18)
$$\frac{\partial \overline{c}}{\partial t} + \overline{u} \frac{\partial \overline{c}}{\partial x} = \left(\operatorname{Pe}^{-1} - \operatorname{Pe} \overline{\chi F} \, \overline{u}^2 \right) \frac{\partial^2 \overline{c}}{\partial x^2} - \alpha \frac{\partial \overline{s}}{\partial t} + \alpha \operatorname{Pe} \overline{u} \, \overline{\Psi F} \, \frac{\partial^2 \overline{s}}{\partial x \partial t}$$

with an error of $O(\epsilon^3)$. The concentration distribution c(X, y, z, T) can be obtained from $\overline{c}(X, T)$. Adding ϵ times Equation (4.8) to $c^{(0)} = \overline{c}^{(0)}$, together with the $O(\epsilon^2)$ terms $-\epsilon^2 \operatorname{Pe}\alpha \frac{\partial \overline{s}^{(1)}}{\partial t} \Psi$ and $\overline{u} \frac{\partial \overline{c}^{(1)}}{\partial x} \chi$:

(4.19)
$$c = \overline{c} + \epsilon \operatorname{Pe}\left(-\alpha \frac{\partial \overline{s}}{\partial T}\Psi + \overline{u} \frac{\partial \overline{c}}{\partial X}\chi\right) + O(\epsilon^2).$$

Reverting to original variables t and x:

(4.20)
$$c = \overline{c} + \operatorname{Pe}\left(-\alpha \frac{\partial \overline{s}}{\partial t}\Psi + \overline{u} \frac{\partial \overline{c}}{\partial x}\chi\right) + O(\epsilon^2).$$

4.2. Kinetics of Adsorption and Desorption

The surface concentration is specified by a kinetic function of the following form:

(4.21)
$$\frac{\partial s}{\partial t} = h(c_w, s, \ldots)$$

where c_w denotes the solute concentration on the wall. Dependence on other parameters that could possibly vary over the capillary wall is indicated by The function h in Equation (4.21) can be expanded in Taylor series around \bar{c} using Equation (4.20):

(4.22)
$$\frac{\partial s}{\partial t} = h(\overline{c}, s, \ldots) + \frac{\partial h}{\partial \overline{c}} \left(-\alpha \frac{\partial \overline{s}}{\partial t} \Psi + \overline{u} \frac{\partial \overline{c}}{\partial x} \chi \right) + O(\epsilon^2).$$

In the applications to be discussed in the next section, a linear kinetics of the form:

(4.23)
$$\frac{\partial s}{\partial t} = h(c_w, s, \lambda, K) = \lambda(Kc_w - s)$$

will be specified, where λ is the rate constant of desorption from the wall and K is the equilibrium constant of the adsorption-desorption process. The combination λK is the rate constant of adsorption. For linear kinetics, $\frac{\partial h}{\partial \overline{c}} = \lambda K$. Therefore, Equation (4.22) for linear kinetics takes the form:

(4.24)
$$\frac{\partial s}{\partial t} + \lambda s = \lambda K \left[\overline{c} + \operatorname{Pe} \left(-\alpha \frac{\partial \overline{s}}{\partial t} \Psi_w + \overline{u} \frac{\partial \overline{c}}{\partial x} \chi_w \right) + O(\epsilon^2) \right].$$

Averaging Equation (4.24) over $\partial \Omega$ and rearranging terms:

(4.25)
$$(1 + \alpha \lambda K \operatorname{Pe} \bar{\Psi}_w) \frac{\partial \bar{s}}{\partial t} + \lambda \bar{s} = \lambda K (\bar{c} + \operatorname{Pe} \bar{u} \frac{\partial \bar{c}}{\partial x} \bar{\chi}_w).$$

Here, it has been assumed that λ and K are uniform on the curve $\partial\Omega$. The notations $\bar{\Psi}_w$ and $\bar{\chi}_w$ indicate Ψ_w and χ_w averaged over $\partial\Omega$. The order of magnitude of neglected terms in Equation (4.25) depends on the magnitude of λK , but is at least $O(\epsilon^2)$.

The asymptotically reduced equations, (Equations (4.18) and (4.25)) can be solved simultaneously to find an asymptotic approximation to the axial distribution of \bar{c} . This, in general, will require numerical integration, but only in one-dimension. An asymptotic approximation for the three-dimensional distribution of c can then be calculated from the axial distribution of \bar{c} , using Equation (4.20). A complete solution of the problem of transport, on the other hand, involves solving Equation (4.1), numerically in three dimensions.

For the purpose of brevity, the former approach will be called the 'asymptotically reduced model' and the latter approach will be called the 'three dimensional model'. Numerical comparisons between results obtained using the two models will be presented in a later section. For now, we proceed to develop from the asymptotically reduced model, a limit important for separations based on the principle of chromatography. This limit is realized when the adsorption and desorption processes on the wall are fast enough to come to a state close to chemical equilibrium, well before the injected plug reaches the detection system. In this limit, analytical expressions directly applicable to dispersion calculations can be obtained.

4.2.1. Fast Adsorption and Desorption: the Chromatographic Limit

For fast adsorption and desorption $\lambda K \sim O(1)$ so the error in Equation (4.25) is of the order $O(\epsilon^2)$ and we can restate Equation (4.25) as:

(4.26)
$$\frac{\partial \bar{s}}{\partial t} + \underline{\lambda}\bar{s} = \underline{\lambda}K\bar{c} + \underline{\lambda}K\text{Pe}\overline{u}\frac{\partial \bar{c}}{\partial x}\chi_w + O(\epsilon^2)$$

where, $\underline{\lambda}$ is defined by :

(4.27)
$$\underline{\lambda} = \frac{\lambda}{1 + \alpha \lambda K \text{Pe}\Psi_w}.$$

The differential equation (4.26) can be integrated directly by using an integrating factor $\exp(\underline{\lambda}t)$. This integration with a perimeter independent initial condition s(x, t = 0) gives:

(4.28)
$$\overline{s} = \overline{s}(x, t = 0) \exp(-\underline{\lambda}t) + \underline{\lambda}KI + \underline{\lambda}K\text{Pe}\overline{u}\chi_w \frac{\partial I}{\partial x} + O(\epsilon^2)$$

where

(4.29)
$$I = \int_0^t \overline{c}(x,\tau) \exp\left[-\underline{\lambda}(t-\tau)\right] d\tau = \int_0^t \overline{c}(x,t-\eta) \exp\left(-\lambda\eta\right) d\eta.$$

In the long time limit $t = T/\epsilon \to \infty$ the integral I becomes

(4.30)
$$I_{\infty} = \int_{0}^{\infty} \overline{c}(x, t - \eta) \exp\left(-\underline{\lambda}\eta\right) d\eta$$

and Equation (4.28) becomes:

(4.31)
$$\bar{s} = \underline{\lambda}KI + \underline{\lambda}K\operatorname{Pe}\overline{u}\bar{\chi}_{w}\frac{\partial I}{\partial x} + O(\epsilon^{2}).$$

The quantity $\overline{c}(x, t - \eta)$ can be expanded in a Taylor series around t to give:

(4.32)
$$I_{\infty} = \sum_{n=0}^{\infty} \frac{(-1)^n}{n!} \frac{\partial^n \overline{c}}{\partial^n t} T_n$$

where $T_n = \int_0^\infty \eta^n \exp\left(-\underline{\lambda}\eta\right) d\eta$. Following evaluation, the integral $T_n = \frac{n!}{\underline{\lambda}^{n+1}}$. Substituting:

(4.33)
$$I_{\infty} = \sum_{n=0}^{\infty} \frac{\partial^n \overline{c}}{\partial^n t} \frac{1}{\underline{\lambda}^{n+1}}.$$

Since in the long time limit $\frac{\partial^n}{\partial t^n} = \epsilon^n \frac{\partial^n}{\partial T^n}$, Equation (4.33) can be considered an asymptotic expansion in ϵ for I_{∞} . Therefore, I_{∞} can be approximated to an error of $O(\epsilon^2)$ by retaining only the first two terms of this series. For approximation of $\frac{\partial I_{\infty}}{\partial x}$, only one term is necessary as in the long time limit $\frac{\partial}{\partial x} = \epsilon \frac{\partial}{\partial X}$.

Inserting the above approximations of I_{∞} into Equation (4.31) we get:

(4.34)
$$\bar{s} = \underline{\lambda}K \left[\frac{1}{\underline{\lambda}}\bar{c} - \frac{1}{\underline{\lambda}^2}\frac{\partial\bar{c}}{\partial t} + O(\epsilon^2)\right] + \underline{\lambda}K \operatorname{Pe}\overline{u}\bar{\chi}_w \left[\frac{1}{\underline{\lambda}}\frac{\partial\bar{c}}{\partial x} + O(\epsilon^2)\right] + O(\epsilon^2).$$

Differentiating Equation (4.34) with respect to t:

(4.35)
$$\frac{\partial \bar{s}}{\partial t} = K \frac{\partial \bar{c}}{\partial t} - \frac{K}{\underline{\lambda}} \frac{\partial^2 \bar{c}}{\partial t^2} + K \operatorname{Pe} \overline{u} \, \bar{\chi}_w \, \frac{\partial^2 \bar{c}}{\partial t \partial x} + O(\epsilon^3)$$

Here, the error term is $O(\epsilon^3)$ because $\frac{\partial}{\partial t} = \epsilon \frac{\partial}{\partial T}$. To estimate the second order time and space derivatives in Equation (4.35) to $O(\epsilon^3)$, an $O(\epsilon^2)$ approximation of $\frac{\partial \overline{c}}{\partial t}$ should be sufficient. To that end we note from Equation (4.35):

(4.36)
$$\frac{\partial \bar{s}}{\partial t} = K \frac{\partial \bar{c}}{\partial t} + O(\epsilon^2).$$

Equation (4.6) can be re-expressed in independent variables t and x and the dependent variable $c = c^{(0)} + O(\epsilon)$ as $\frac{\partial \overline{c}}{\partial t} + \overline{u} \frac{\partial \overline{c}}{\partial x} = -\alpha \frac{\partial s}{\partial t} + O(\epsilon^2)$. Using Equation (4.36) in this relationship we get after rearrangement:

(4.37)
$$\frac{\partial \overline{c}}{\partial t} = -\frac{\overline{u}}{1+\alpha K} \frac{\partial \overline{c}}{\partial x} + O(\epsilon^2).$$

Differentiating this equation with respect to t and x we get the following expressions for $\frac{\partial^2 \overline{c}}{\partial t^2}$ and $\frac{\partial^2 \overline{c}}{\partial t \partial x}$:

(4.38a)
$$\frac{\partial^2 \overline{c}}{\partial t^2} = \frac{\overline{u}^2}{\left(1 + \alpha K\right)^2} \frac{\partial^2 \overline{c}}{\partial x^2} + O(\epsilon^3)$$

(4.38b)
$$\frac{\partial^2 \overline{c}}{\partial x \partial t} = -\frac{\overline{u}}{(1+\alpha K)} \frac{\partial^2 \overline{c}}{\partial x^2} + O(\epsilon^3).$$

When Equations (4.38a) and (4.38b) are used in Equation (4.35) and $\underline{\lambda}$ is replaced using Equation (4.27):

(4.39)
$$\frac{\partial \bar{s}}{\partial t} = K \frac{\partial \bar{c}}{\partial t} - \left[\frac{K}{\lambda (1 + \alpha K)^2} + \left(\frac{\alpha K^2 \Psi_w}{(1 + \alpha K)^2} + \frac{K \chi_w}{(1 + \alpha K)} \right) \operatorname{Pe} \right] \overline{u}^2 \frac{\partial^2 \bar{c}}{\partial x^2} + O(\epsilon^3).$$

The quantity $\frac{\partial^2 \overline{s}}{\partial x \partial t}$ appearing in Equation (4.18) can be calculated from Equation (4.36). Using Equation (4.38b):

(4.40)
$$\frac{\partial^2 \overline{s}}{\partial x \partial t} = -\frac{K}{(1+\alpha K)} \overline{u} \frac{\partial^2 \overline{c}}{\partial x^2} + O(\epsilon^3)$$

Using Equations (4.39) and (4.40) in Equation (4.18) we get:

(4.41)
$$\frac{\partial \overline{c}}{\partial t} + A\overline{u}\frac{\partial \overline{c}}{\partial x} = D_{eff}\frac{\partial^2 \overline{c}}{\partial x^2}$$

where:

(4.42a)
$$A = \frac{1}{(1+K')}$$

(4.42b)
$$D_{eff} = \frac{\operatorname{Pe}^{-1}}{1+K'} + \left[-\frac{\overline{\chi F}}{1+K'} - 2\frac{K'\overline{\Psi F}}{(1+K')^2} + \frac{K'^2\overline{\Psi}_w}{(1+K')^3} \right] \operatorname{Pe}\overline{u}^2 + \frac{K'}{\lambda(1+K')^3}\overline{u}^2.$$

Here, $K' = \alpha K$. In the above, the following relationship derived in Appendix B has been used:

(4.43)
$$\overline{\Psi F} = -\overline{\chi}_w$$

The first term is dispersion due to molecular diffusion. The molecular diffusivity is scaled by a factor of 1 + K indicating that the solute can diffuse molecularly only for the fraction of time it spends in the mobile phase. The second and third terms in the expression for D_{eff} in Equation (4.42b) are present only in a cross-sectionally nonuniform flow as for uniform flow F = 1, we get $\chi = 0$ from Equation (4.10) and $\overline{\Psi F} = \overline{\psi} = 0$ from Equation (4.11). The term with the coefficient $\overline{\chi F}$ is a consequence of shear-induced dispersion [9, 10] and is present even when adsorption-desorption is absent on the wall, but now, it is scaled by the factor 1 + K. The second term represents dispersion due to coupling between adsorptiondesorption and axial convection. The last two terms are pure adsorption-desorption effects, being present, even in an uniform flow. If the wall interaction was assumed to proceed at an infinitely fast rate, the last term would not appear. It quantifies a reaction kinetic effect on band broadening. In passing, we can note the correspondence between Equation (4.42b) and the general form Equation (2.19) mentioned while covering the background material in Section 2.10.

For a given flow type and geometry, the coefficients $\overline{\Psi}_w$, $\overline{\Psi F}$, $\overline{\chi}_w$, $\overline{\chi F}$ can be obtained by solving Equations (3.9) and (4.10), either analytically and numerically. The calculated coefficients for pressure-driven flow (see Table 4.1) in some representative microchannel crosssections are shown in Table 4.2.

4.3. Applications

In this section the functions Ψ and χ and their statistics $\overline{\Psi}_w, \overline{\chi}_w$, $\overline{\Psi}\overline{F}$ and $\overline{\chi}\overline{F}$ will be calculated for various geometries, flow and adsorption patterns that are important to microfluidic separation systems, as well as to the problems used in the following sections to test the asymptotically reduced model. The calculated values of $\overline{\Psi}_w, \overline{\chi}_w, \overline{\Psi}\overline{F}$ and $\overline{\chi}\overline{F}$ can be used:

- (i) to calculate the coefficients in Equations (4.18) and (4.25) to be solved in the asymptotically reduced model
- (ii) for the calculation of effective dispersion coefficient using Equation (4.42b) in case of chromatographic separations.

The knowledge of the full distribution of functions Ψ and χ can be used to calculate the spatial distributions of c using Equations (4.20), after the \overline{c} distribution has been calculated by solving Equations (4.18) and (4.25).

4.3.1. Influence of Wall Interactions

There are situations of practical importance when the boundary value problem for Ψ can be further simplified. Two such situations will be discussed below. In either cases, the effect of adsorption in Equations (4.18), (4.22) and (4.20) can be modeled with geometrically calculated quantities.

4.3.1.1. Uniform Wall Interactions. In majority of applications in CE and open-channel CEC, the wall is composed of or coated with the same material [72, 75, 52]. The kinetic

coefficients of any adsorption-desorption process will be homogenous on the wall under this condition. The rate of change of adsorbed surface concentration is determined solely by the wall volumetric concentration c_w and adsorbed surface concentration s of a single species. Thus, the wall reaction kinetics can be represented by the function $h(c_w, s)$, such that $\frac{\partial s}{\partial t} = h(c_w, s)$.

To leading order, this results either in $h(\overline{c}^{(0)}, s^{(0)}) = 0$ for fast adsorption-desorption (when *h* is order one), or $\frac{\partial s^{(0)}}{\partial t} = h(\overline{c}^{(0)}, s^{(0)})$ for slow adsorption-desorption (when *h* is order ϵ). Assuming s(t = 0) was uniform over $\partial\Omega$, we can conclude that $s^{(0)}$ is uniform over $\partial\Omega$ at all times. In other words, $s^{(0)} = \overline{s}^{(0)}$ and $\frac{\partial s^{(0)}}{\partial t} = \frac{\partial \overline{s}^{(0)}}{\partial t}$. Thus, the right hand side of Equation (4.9b) specializes to $\frac{1}{\alpha}$:

(4.44a)
$$\nabla_{\Omega}^{2}\Psi = 1$$

(4.44b)
$$\nabla_{\Omega} \Psi \cdot \hat{\mathbf{n}} = \frac{1}{\alpha}$$

$$(4.44c) \qquad \overline{\Psi} = 0$$

In this case, Ψ will be determined solely from the geometry of the cross-section. Ψ calculated for various cross-sections are reported in Table 4.2. The function Ψ can be obtained analytically in rectangular cross-sections by solving the 2-D boundary value problem in Equation (4.11) [**76**]. For square cross-section, the function Ψ is shown in Table 4.2. The results for trapezoidal cross-section were calculated using a commercially available package (Matlab PDE Toolbox) employing the finite element method [**77**]. The ψ calculated in the trapezoidal geometry is shown in Figure 4.3(b). **4.3.1.2.** Nonuniform Wall Interactions. If the kinetic coefficients of the adsorptiondesorption process has a variation across the cross-section then the last mentioned simplification to the right hand side of Equation (4.9b) cannot be made. However, there are situations of relevance to transport in etched capillaries with cover slides [59] and to the process of shear-driven chromatography [78] where the influence of wall kinetics can be easily modeled from geometry as follows. If the boundary $\partial\Omega$ can be divided into n segments $\partial\Omega_i$ of length l_i (where i = 1 to n) such that material properties affecting adsorption-desorption and initial conditions on s are constant on each segment (but can vary between the segments), we could multiply Equation (4.11) by $\frac{\partial\overline{s}}{\partial t} = \sum_{i=1}^{n} \frac{l_i}{P} \frac{\partial s_i}{\partial t}$ (where $P = \sum_{i=1}^{n} l_i$) to get the following boundary value problem for the function $\Psi_s = \frac{\partial\overline{s}}{\partial t} \Psi$:

(4.45a)
$$\nabla_{\Omega}^{2}\Psi_{s} = \frac{\partial \overline{s}}{\partial t} = \sum_{i=1}^{n} \frac{l_{i}}{P} \frac{\partial s_{i}}{\partial t}$$

(4.45b)
$$\nabla_{\Omega}\Psi_s \cdot \hat{\mathbf{n}} \mid_{\partial\Omega_j} = \frac{1}{\alpha} \frac{\partial s_j}{\partial t} \text{ where } j = 1 \text{ to } n$$

(4.45c)
$$\overline{\Psi_s} = 0.$$

where, from Equation (4.20) Ψ_s is used in calculating c from \overline{c} as follows:

(4.46)
$$c = \overline{c} + \operatorname{Pe}\left(-\alpha\Psi_s + \overline{u}\frac{\partial\overline{c}}{\partial x}\chi\right) + O(\epsilon^2).$$

Equation (4.45b) represents the *n* boundary conditions at *n* segments of the boundary curve $\partial \Omega$. The problem in Equation (4.45) can be simplified by the principle of superposition,

leading to the definition of the functions ψ_i as follows:

(4.47)
$$\Psi_s = \frac{\partial \overline{s}}{\partial t} \Psi = \sum_{i=1}^n \frac{l_i}{P} \frac{\partial s_i}{\partial t} \psi_i.$$

The boundary value problem for each ψ_i is of the following form:

(4.48a)
$$\nabla_{\Omega}^{2}\psi_{i} = 1$$

(4.48b)
$$\nabla_{\Omega}\psi_{i}\cdot\hat{\mathbf{n}}\mid_{\partial\Omega_{j}}=\frac{1}{\alpha}\delta_{ij} \text{ where } j=1 \text{ to } n$$

(4.48c)
$$\overline{\psi_i} = 0$$

where $\delta_{ij} = 1$, when i = j and 0 otherwise. Therefore:

(4.49)
$$c = \overline{c} + \operatorname{Pe}\left(-\alpha \sum_{i=1}^{n} \frac{l_i}{P} \frac{\partial s_i}{\partial t} \psi_i + \overline{u} \frac{\partial \overline{c}}{\partial x} \chi\right) + O(\epsilon^2).$$

It can be noted here, that n should be interpreted as number of active segments of the wall. A segment of the wall is inactive if it does not adsorb the solute at all. The l_i from that segment does not appear in the calculation of P, α and \overline{s} . Therefore, it is not necessary to define ψ_i for inactive segments for use in Equation (4.49).

Example: The gap between parallel planes can be used to approximate the microfluidic channels used in shear-driven chromatography [79] (Figure 4.1(a)) and electroosmotic micropumping [80] (Figure 4.1(b)). To obtain $\bar{\psi}_w$ care should be taken to account for the fact that shear-driven chromatography and chromatography with electroosmotic micro-pumping employ an adsorptive coating only on the passive (electrode-free [79] or stationary [81]) wall. If the width of the channel is chosen as w_0 , $\alpha = 1$ since only the active perimeter is used in the calculations, unlike for homogeneous adsorption where $\alpha = 2$ (see Table 4.2). Equation (4.48) needs to be solved for a single function ψ whose gradient equals -1 on the active wall (say, top wall at y = 1/2) and 0 on the inactive wall at (say, bottom wall at y = -1/2). Also, there is only one active segment, so l/P = 1 in Equation (4.49). Then the function ψ evaluates to $\frac{1}{2}y^2 - \frac{1}{2}y + \frac{1}{24}$. However, $\bar{\psi}_w = \frac{1}{12}$, the same value as in Table 4.2. For dispersion calculations in shear-driven chromatography, it may be noted that the inhomogeneous pattern of adsorption makes the same contribution through $\bar{\psi}_w = \frac{1}{12}$ in Equation (4.42b), as would be the case if the wall interactions were uniform at each cross-section.

4.3.2. Influence of Inhomogeneous Flow Fields

Homogeneous flow fields do not cause dispersion by the Taylor-Aris mechanism [9, 10]. Here, the method of calculation of the function χ and the metrics $\overline{\chi}_w$ and $\overline{\chi}\overline{F}$ will be described using several inhomogeneous flow fields of importance in microfluidics. The flow fields to be discussed are homogeneous in the axial direction and are obtained as solutions to the fluid momentum and continuity equations under appropriate condition and in the fully developed limit [49]. The solution will always be normalized to satisfy $\overline{F} = 1$. The following flow patterns will be discussed:

(i) A purely pressure-driven flow profile (F_p) , which can represent the flow field in gas chromatography [29] and liquid chromatography [30] and is also used for the lubrication theory representation of axially variable electroosmotic flow in CE and CEC in the thin Debye layer limit (refer to [15] and Chapter 3)

Geometry	F_p
Parallel Plate	$3/2(1-4y^2)$
Cylinder	$2(1-r^2)$
Rectangle	$u_p(y,z)/\overline{u}_p$ from Equation (3.20), (3.21) and (3.22)
1:2 Trapezoid	Calculated numerically, see Figure 4.3(a)

Table 4.1: The flow distribution function F for pressure-driven flow in a plane channel, cylinder, rectangle and trapezoid. The co-ordinate y for the plane channel is measured from the axis of the channel in units of channel width, the radial co-ordinate r for the cylinder is measured in units of capillary radius. The coordinates y and z for rectangular channel is as shown in Figure 3.1.

- (ii) An electrokinetic flow profile (F_{κ}) when the Debye layers have finite thickness or the Debye-Hückel parameter $\kappa = 1/\lambda_D$ is non-infinitesimal. The Debye-Hückel approximation [1] will be used. This commonly happens in nanochannels and leads to a nonuniform flow profile capable of significant solute dispersion.
- (iii) A shear or 'Couette' flow profile (F_s) set forth either by boundary motion (sheardriven chromatography [79]) or by zeta potential variation over $\partial\Omega$ (e.g. due to the use of cover-slips [59]) in the thin Debye layer limit. The flow field in separations by circular chromatography with AC electroosmotic micro-pumping [81] can also be represented by this flow profile.

In the following discussion, the shape function for the χ will be subscripted with one of the subscripts p, κ and s to emphasize the flow type it corresponds to. The symbol 'p' stands for the pressure drive characterizing the flow shape F_p , ' κ ' stands for non-infinitesimal Debye-Hückel parameter κ characterizing F_{κ} and 's' stands for the boundary-generated shear characterizing F_s . The use of our method to calculate dispersion in various cross-section relevant to microfluidics will be demonstrated with respect to the pressure-driven flow case.



(a) Shear-Driven Chromatography



(b) Electroosmotic Micro-pump

Figure 4.1: Schematic of Shear-Driven Chromatography and AC Electroosmotic Micro-pumping in a Plane Channel. The flow profile in either situations can be approximated by a 'Couette Flow'. In case of an electroosmotic micropump, the flow disturbance in a small region near the electrodes, such as the streamline shown in Figure 4.1(b) has been ignored. For chromatographic applications [79, 81], the bottom surface of either devices is coated with a wall retentive material.



Figure 4.2: Contours of the function χ for a channel of square cross-section.



Figure 4.3: The flow profile function F_p (Figure 4.3(a)) for pressure driven flow, and the functions Ψ (Figure 4.3(b)) and χ (Figure 4.3(c)) numerically obtained for an isosceles trapezoid of height b and width 2b. The functions are symmetric about a vertical axis passing through the centroid of the trapezoid. In Figure 4.3(a), the values represented by the iso-lines decreases outward in steps of 0.2 from the innermost iso-line shown (the iso-line closest to the centroid) with value 2. In Figure 4.3(b), the values represented by the iso-lines increases outward in steps of 0.04 from the innermost iso-line shown (the iso-line shown (the iso-line shown (the iso-line shown (the iso-line shown in steps of 0.02 from the innermost iso-line shown (the iso-line shown (the iso-line shown (the iso-line shown (the iso-line shown in steps of 0.02 from the innermost iso-line shown (the iso-line shown iso-line shown (the iso-line shown)

4.3.2.1. Pressure-driven Flow in Various Cross-Sections. The flow profile in a purely pressure-driven flow can be represented without loss of generality by $F_p = \mathcal{P}/\bar{\mathcal{P}}$ where, \mathcal{P} is defined in the same way, as in [15], viz.:

(4.50a)
$$\nabla_{\Omega}^{2} \mathcal{P} = 1$$

(4.50b)
$$\mathcal{P}|_{\partial\Omega} = 0.$$

The flow profile F_p calculated for channels of various cross-section are shown in Table 4.1. The corresponding χ calculated by solving Equation (4.10) in plane, rectangular, round and trapezoidal channels are reported in Table 4.2. The analytical expression for the function χ_p that can be calculated by solving Equations (4.10) with a pressure-driven flow field in a rectangle of width $w_0 = 2b$ and height 2c (Figure 3.1) is as follows:

(4.51)
$$\chi_p = \frac{1}{\overline{\mathcal{P}}} \sum_{p=0}^{\infty} \sum_{q=0}^{\infty} F_{pq} \cos \frac{p\pi(y+b)}{b} \cos \frac{q\pi(z+c)}{c}$$

(4.52a)
$$F_{00} = 0$$

(4.52b)
$$\left[\left(\frac{\pi}{b}\right)^2 + \left(\frac{\pi}{c}\right)^2 \right] F_{pq} = W_{pq} \text{ for } p, q \in I ; \ (p,q) \neq (0,0)$$

where:

(4.53a)
$$W_{pq} = \frac{256b^3c}{\pi^5} \sum_{n=0}^{\infty} \frac{\tanh\left[\frac{(2n+1)\pi a}{2b}\right]}{(2n+1)\left[(2n+1)^2 - 4q^2\right]\left[(2n+1)^2a^2 + 4b^2p^2\right]}$$

(4.53b)
$$W_{0q} = \frac{2b^2}{\pi^2 q^2} \left\{ 1 + \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{q^2}{(2n+1)^2 \left[(2n+1)^2 - 4q^2\right]} \left[\frac{\tanh\left[\frac{(2n+1)\pi b}{2c}\right]}{\frac{(2n+1)\pi b}{2c}} \right] \right\}.$$

In Equation (4.53a), p = 1 to ∞ and q = 0 to ∞ . In Equation (4.53b), q = 1 to ∞ . The quantity $\bar{\mathcal{P}}$ required in Equation (4.51) is the cross-sectional average of the function $\mathcal{P} = (u_p)/(2b)^2$ calculated for pressure-driven by Equation (4.50) and has been calculated in [15, 82]:

(4.54)
$$\bar{\mathcal{P}} = \frac{1}{3} - 2\frac{b}{c} \left(\frac{2}{\pi}\right)^5 \sum_{n=0}^{\infty} \frac{1}{(2n+1)^5} \tanh\left[(2n+1)(\pi c/2b)\right].$$

Equation (4.51) was obtained by adapting the solution of a similar problem in [83] to the current notation and non-dimensionalization scheme. The contours of function χ for square cross-section (b = c) is shown in Figure 4.2.

The flow F_p and the shape function χ for the trapezoidal cross-section, are shown in Figures 4.3(a) and 4.3(c), respectively. The relevant calculations were performed using a commercially available package (Matlab PDE Toolbox) that employs the finite element method [77].

Section 4.4.1 will involve a numerical study on transport in circular cylinders in presence of a pressure-driven flow and a purely adsorptive process on the wall.

4.3.2.2. Electrokinetic Flow with Finite Debye Layers. The electroosmotic flow profile F_{κ} in a microchannel, in the presence of finite Debye layers, when all points on the wall have the same zeta potential is geometrically similar to the distribution of electric potential Φ , as described in Section 2.2. Under the Debye-Hückel approximation $(e\zeta/K_bT < 1)$, Equations (2.6) and (2.10) of Chapter 2 are available for calculation of the electric potential and flow fields respectively. Scaling the linear dimensions of the microchannel with w_0 and the electric potential with ζ_0 we get:

(4.55a)
$$F_{\kappa} = (\Phi - \mathcal{Z})/(\bar{\Phi} - \mathcal{Z})$$

(4.55b)
$$\nabla_{\Omega}^{2}\Phi - \kappa^{\prime 2}\Phi = 0$$

$$(4.55c) \qquad \qquad \Phi|_{\partial\Omega} = 1$$

where

(4.56)
$$\kappa' = w_0 / \lambda_D = w_0 \left[\frac{8\pi e^2 n(\infty)}{\kappa k_B T} \right]^{\frac{1}{2}}.$$

Equations (4.55b) and (4.55c) have been solved analytically and quantities $\overline{\chi_{\kappa w}}$, $\overline{\chi_{\kappa} F_{\kappa}}$ has been calculated numerically in Section 4.4.2.5 for channels with square cross-section (Table 4.5).

4.3.2.3. Shear Flow. We consider flow profiles of the form $F_s = \mathcal{E}/\bar{\mathcal{E}}$, where \mathcal{E} has the same definition in [15], viz.:

(4.57a)
$$\nabla_{\Omega}^{2} \mathcal{E} = 0$$

(4.57b)
$$\mathcal{E}|_{\partial\Omega} = \mathcal{Z}$$

where \mathcal{Z} is the dimensionless slip velocity and can vary over $\partial \Omega$.

The \mathcal{Z} distribution can represent zeta potential variation over $\partial\Omega$, as may arise from the use of glass cover-slides bonded to a micro-patterned PDMS substrate[59], or, from the

Channel Cross-section	Gap between Parallel Plates	Circular	Square	1:2 Isosceles Trapezoid
α	2	2	4	$2+\sqrt{2}$
Ψ	$\frac{y^2}{2} - 1/24$	$\frac{1}{8}(2r^2-1)$	$\frac{1}{4}(y^2+z^2)-\frac{1}{24}$	Figure 4.3(b)
χ	$-\frac{y^4}{2}+\frac{y^2}{4}-\frac{7}{480}$	$-\frac{r^4}{8} + \frac{r^2}{4} - \frac{1}{12}$	Figure 4.2, Equation (4.51)	Figure 4.3(c)
$\overline{\Psi}_w$	$\frac{1}{12}$	$\frac{1}{8}$	$\frac{1}{24}$	0.113
$\overline{\chi}_{pw} / - \overline{\Psi F_p}$	$\frac{1}{60}$	$\frac{1}{24}$	0.0155	0.052
$-\overline{\chi_p F_p}$	$\frac{1}{210}$	$\frac{1}{48}$	0.0084	0.0329

Table 4.2: The functions Ψ and χ and the coefficients α , $\overline{\Psi}_w$, $\overline{\Psi F}$, $\overline{\chi}_w$, $\overline{\chi F}$ for pressure-driven flow (see Table 4.1) in a plane channel and in channels with circular, square and trapezoidal cross-section. The co-ordinate y for parallel plate is measured from the axis of the channel in units of channel width. The radial co-ordinate r for the circular cross-section is measured in units of the radius. The co-ordinates y and z for a square are as defined in Figure 3.1. The isosceles trapezoid has altitude w_0 and half of the sum of its parallel sides equals $2w_0$, see Figure 4.3. The Ψ and χ distributions for the trapezoid is obtained numerically.

$$\begin{array}{c|c|c} F_s & 2(y+1) \\ \chi_s & \frac{y^3}{3} - \frac{y}{4} \\ \overline{\chi}_{sw} & \frac{1}{12} \\ -\overline{\chi_s F_s} & \frac{1}{30} \end{array}$$

Table 4.3: The function χ_s and the coefficients $\overline{\chi}_{sw}$ and $\overline{\chi_s F_s}$ for Shear Flow $F_s = \mathcal{E}/\overline{\mathcal{E}}$ in a plane channel. The co-ordinate y is measured from the axis of the channel in units of channel width. On $y = \frac{1}{2}$ and $y = -\frac{1}{2}$, $\mathcal{E} = 1$ and $\mathcal{E} = 0$, respectively.

electrodes embedded on the wall in an AC electroosmotic micro-pump. It can also represent the motion of parts of the boundary (e.g. the moving wall in shear-driven chromatography, [79]). The shape function calculation to be described is particularly relevant to a novel chromatographic separation that was carried out in a microchannel with the flow driven by AC electroosmotic micro-pumps [81]. As a specific example, we consider the gap w_0 between two parallel plates and $\mathcal{E} = \mathcal{Z}_t = 1$ on the top boundary $(y = \frac{1}{2})$ and $\mathcal{E} = \mathcal{Z}_b = 0$ on the
bottom boundary $(y = -\frac{1}{2})$. Table 4.3 has been constructed with the solution of Equations (4.57) and (4.10) followed by calculation of $\overline{\chi}_{sw}$ and $-\overline{\chi_s F_s}$.

4.3.3. Band broadening in chromatography

The study of dispersion in the chromatographic limit is one of the most important application of the shape function based approach developed here. It is more common in the literature on chromatography and electrochromatography [28, 25, 84] to use a quantity with dimensions of length known as Height equivalent of Theoretical Plate (HETP) to quantify the band broadening effects in the separation. This quantity can be defined as the incremental change in the variance of the solute distribution per unit length of migration of its center of mass [28]. It can be calculated in terms of D_{eff} as follows [25]:

where the asterisk denotes that we have reverted to dimensional quantities. If the adsorptiondesorption kinetics is linear, the dimensional form of Equation (4.42b) can be used in Equation (4.58) to get:

(4.59)
$$\operatorname{HETP} = 2\frac{D^*}{\overline{u}^*} + C_m \frac{\overline{u}^* w_0^2}{D^{*2}} + C_\lambda \overline{u}^* w_0$$

where C_m known as the 'resistance to mass transfer in the mobile phase' [25] is:

(4.60)
$$C_m = 2\left(-\overline{\chi F} - \frac{K'\overline{\Psi F}}{(1+K')} + \frac{K'^2\overline{\Psi}_w}{(1+K')^2}\right)$$

Mode	Flow	C_m	Reference
Electrochromatography	EOF in TDL limit (Uniform)	$\frac{K^{\prime 2}}{6(1+K^{\prime})^2}$	[84]
Liquid/Gas Chromatography	Pressure-driven Flow	$\frac{51K'^2 + 18K' + 2}{210(K'+1)^2}$	[28]
Shear-driven Chromatography	Couette Flow	$\frac{2{+}14K'{+}32K'^2}{30(K'{+}1)^2}$	[79]

Table 4.4: Calculation of the Resistance to Mass Transfer in the Mobile Phase for Various Open Channel Modes of Chromatography in Plane Channels.

and C_{λ} is the 'resistance to mass transfer due to finite adsorption-desorption rate' calculated by:

(4.61)
$$C_{\lambda} = \frac{2K'}{\lambda^*(1+K')^2} \overline{u}^* w_0.$$

The term $C_{\lambda} = \frac{K'}{6\lambda^*(1+K')^2}$ is a consequence of the adsorption-desorption process and does not depend on the specific flow field used in a chromatographic separation. The calculation of C_m depends on the flow field and will now be specialized to the geometry of plane channel to illustrate the use of the method developed here in band broadening calculations. The $\overline{\Psi}_w, \overline{\Psi F}$ and $\overline{\chi F}$ values for plane channel are obtained from Table 4.2. Table 4.4 shows the values of C_m calculated with Equation (4.60) for three different chromatographic separation techniques agree with results previously derived in the literature using other methods. The $\overline{\chi F}$ and $\overline{\chi}_w$ for dispersion calculation in shear-driven chromatography is available from Table 4.3; Table 4.2 can be used for calculating $\overline{\Psi}_w$, by virtue of the discussion the end of Section 4.3.2. The calculation of C_m using Equation (4.60) was also performed for circular capillaries and checked for agreement with results available in the literature [**28**, **25**].

4.4. Numerical Comparisons

In this section several test problems will be solved numerically in order to ascertain the accuracy of the asymptotic theory. A irreversible adsorption process and a reversibleadsorption desorption will be studied and there will be two different types of channel crosssections involved viz. circular and square. The flow fields in the test problems involved will represent pressure drive, electrokinetic drive in microchannels and electrokinetic drive in nanochannels.

4.4.1. Slow Irreversible Adsorption in a Circular Capillary

We will study slow irreversible adsorption in a circular capillary. This problem allows easy closure of Equation (4.18) and Equation (4.20) and is a prototype of protein adsorption problems in separations that result in sample loss [20, 19].

4.4.1.1. Theory of Slow Irreversible Adsorption. A first order irreversible adsorption process follows the kinetic law:

(4.62)
$$\frac{\partial s}{\partial t} = \beta c_w$$

where β is the adsorption coefficient. We require β to be $O(\epsilon)$, for our asymptotic theory to be valid and for the purpose of studying the interesting limit where the adsorption time scale is comparable to the migration time scale [**31**].

Equation (4.62) is substituted in Equation (4.18) and following use of Equation (4.64) to replace c_w with \overline{c} we get:

(4.63a)
$$\frac{\partial \overline{c}}{\partial t} + A\overline{u}\frac{\partial \overline{c}}{\partial x} + B\overline{c} = D_{eff}\frac{\partial^2 \overline{c}}{\partial x^2}$$

(4.63b)
$$B = \alpha\beta - \alpha^2\beta^2 \operatorname{Pe}\overline{\Psi}_w$$

(4.63c)
$$A = 1 + \alpha\beta \operatorname{Pe}\left(\overline{\chi}_w - \overline{\Psi F}\right)$$

(4.63d)
$$D_{eff} = -\mathrm{Pe}^{-1} + \mathrm{Pe}\overline{\chi F}\bar{u}^2.$$

Further, substituting the perimetric average of Equation (4.62) in Equation (4.20) and with the replacement of \bar{c}_w with $\bar{c} + O(\epsilon)$ in the $O(\epsilon)$ accurate second term of Equation (4.20), we get:

(4.64)
$$c = (1 - \alpha\beta \operatorname{Pe}\Psi)\overline{c} + \operatorname{Pe}\overline{u}\frac{\partial\overline{c}}{\partial x}\chi + O(\epsilon^2).$$

Some results to be used for the numerical validation are derived below with the help of method of moments [10]. If equation (4.63a) is integrated with respect to x in $(-\infty, \infty)$ we get the following expression for the total amount of solute $\langle c \rangle = \int_{-\infty}^{\infty} \overline{c} \, dx$ in the capillary:

(4.65)
$$\frac{\partial \langle c \rangle}{\partial t} + B \langle c \rangle = 0$$

where $B = \alpha \beta - \alpha^2 \beta^2$ Pe from Equation (4.63b).

Denoting the concentration at t = 0 as $\langle c \rangle_{t=0}$ and integrating the above equation we get:

(4.66)
$$\langle c \rangle = \langle c \rangle_{t=0} \exp\left(-B t\right).$$

The coefficient B is a loss coefficient. The first term in the right hand side of Equation (4.63b) alone would stand for the loss of solute as if a volumetric rather than surface adsorption was taking place and the second term is a correction to this as the loss occurs on only the wall

where the concentration is different from the mean concentration, as given by Equation (4.64) below.

Multiplying Equation (4.63a) with x and integrating with respect to x in $(-\infty, \infty)$, we get the following expression for the speed $v_{\rm CM}$ of the center of mass of the distribution, after use of (4.65) :

(4.67)
$$v_{\rm CM} = \frac{d}{dt} (x_{\rm CM}) = A\overline{u} = \left[1 + \alpha\beta \operatorname{Pe}\left(\overline{\chi}_w - \overline{\Psi}\overline{F}\right)\right]\overline{u}$$

where $x_{\rm CM} = \frac{\int_{-\infty}^{\infty} x \bar{c} dx}{\int_{-\infty}^{\infty} \bar{c} dx}$. For pressure-driven flow and weak irreversible adsorption, the center of mass of concentration distribution is advected with a mean speed greater than the mean speed of the flow [68]. This speeding up effect occurs at $O(\epsilon)$ in the analysis unlike the chromatographic retention effect for fast reaction discussed in last section which occurs at O(1).

Multiplying Equation (4.63a) with x^2 and integrating with respect to x in $(-\infty, \infty)$ and using $\frac{d}{dt}(x_{\rm CM}) = A$ we get for rate of growth of the variance $\sigma^2 = \frac{\int_{-\infty}^{\infty} (x - x_{\rm CM})^2 \bar{c} dx}{\int_{-\infty}^{\infty} \bar{c} dx}$:

(4.68)
$$\frac{d}{dt}\sigma^2 = 2D_{eff} = 2\left(\operatorname{Pe}^{-1} - \operatorname{Pe}\overline{\chi F}\overline{u}^2\right).$$

The effective dispersion coefficient D_{eff} is a combination of Taylor-Aris (shear-induced) dispersion and molecular diffusion. No effect of the weak adsorption process appears in the effective dispersion coefficient up to two terms in the asymptotic expansion $c = c^{(0)} + \epsilon c^{(1)} + O(\epsilon^2)$.

To specialize these results for numerical comparison in a circular capillary, we choose the radius of the capillary as the radial unit w_0 and use $\alpha = 2$, $\overline{\Psi F} = \frac{1}{12}$ and $\overline{\chi F} = \frac{1}{48}$. Further, the functions $\Psi = \frac{1}{8}(2r^2 - 1)$ and $\chi = -\frac{1}{8}r^4 + \frac{1}{4}r^2 - \frac{1}{12}$ from Table 4.2. The values of A and B

calculated in this analysis for circular capillaries are in quantitative agreement with values predicted by alternative analytical approaches of [68, 69].

4.4.1.2. Numerical Methods. The numerical setup is substantially similar to that used in [52]. The equations of mass transfer Equation (4.1) were discretized in cylindrical polar coordinates using second order differencing [77] and integrated in time with a fourth order Runge-Kutta scheme [85]. The length of the numerical domain was L = 250R, where R is the radius of the channel. Periodic boundary conditions were used at the inlet and the outlet of the channel. The numerical grid spacing used was $\Delta x = \Delta r = 0.025$. For meaningful comparison with results derived for infinitely long cylinder in the last subsection, the end concentrations were not allowed to reach values larger than $c/c_0 = 10^{-10}$.

4.4.1.3. Numerical Results. In the following, $\overline{\Psi F}$, $\overline{\Psi}_w$ and $\overline{\chi F}$ for cylindrical capillaries found from Table 4.2 will be used to calculate the predictions of the asymptotic model on the effective loss coefficient *B* using Equation (4.63b), effective advection coefficient *A* using Equation (4.67) and the effective dispersion coefficient D_{eff} using Equation (4.68) for several values of the reaction rate constant β . The values of *A*, *B* and *C* in the long time limit can also be extracted from the numerical results on loss of sample, motion of center mass and the variance for each value of β . The theoretical and numerical predictions will be compared. The combination β Pe in presenting numerical results β Pe will characterize the ratio of the characteristic radial diffusion time to the characteristic reaction time. Numerical simulations were performed for two Peclet numbers Pe = 5 and 10.

Figure 4.4 shows the exponential decay with time of the fraction of solute within the system calculated by numerical simulation and using Equation (4.66) with B calculated by the asymptotic formula in Equation (4.63b). Figure 4.5 shows BPe, the rate constant of this decay (normalized by a radial diffusion rate constant) calculated from numerical results

and from Equation (4.63b) for various values of β Pe. The asymptotic theory is in good agreement with numerical results in both figures, even for reasonably large values of β Pe. The dependent variable *B*Pe expressed as a function of β Pe does not have any explicit dependence on Peclet number. This is responsible for the collapse of the numerical data from simulations with two different Pe in Figure 4.5.

Figure 4.6 indicates the β dependence of center of mass speed $v_{\rm CM}$ or $A\overline{u}$, calculated by the asymptotic theory and numerical approaches for Pe = 5 and Pe = 10. The theory is accurate for small β Pe values, but discrepancies show up at somewhat smaller value of β than in Figure 4.5.

Figure 4.7 shows that the β dependence of dispersion coefficient cannot be resolved by the asymptotic theory for slow irreversible adsorption. The error incurred on using Equation (4.68), as predicted by the asymptotic theory in place of the numerically observed value of the normalized dispersion measure plotted on the ordinate is about 5% for β Pe = 1. The normalized dispersion measure on the ordinate is designed to emphasize the effect of adsorption on dispersion coefficient over and above the dispersion present due to the parabolic flow profile and to collapse the numerical data for the two Peclet numbers Pe = 5 and Pe = 10. The number 48 in the ordinate of Figure 4.7 is actually $-\frac{1}{\chi F}$ for cylindrical geometry (see Table 4.2).

4.4.2. Dispersion in a rectangular channel with wall interaction

In order to ascertain the accuracy of the asymptotic reduction, three specific test problems will be solved in this section, simultaneously by the asymptotically reduced model (Equations (4.20) and (4.25)) and the three-dimensional model (Equation (4.1)). The former requires solution of a one-dimensional partial equation and the latter requires solution of a

three-dimensional partial differential equation. Both problems are coupled to an ordinary differential equations representing the wall reaction kinetics. Equation (4.20) is used in the asymptotically reduced model to calculate c from \overline{c} ; the three-dimensional model solves for c directly.

4.4.2.1. Test Problems. The test problems pertain to transport of the solute under electroosmotic flow. Additionally, the following specific conditions common to all the test problems to be described will be assumed:

- (i) The microchannel has an axially invariant square cross-section of side 2b. Therefore, the geometric constant $\alpha = 4$, on choosing $w_0 = 2b$.
- (ii) The wall reaction is of the linear form (Equation (4.23)) with λ and K invariant on the wall.
- (iii) Initially, there is no wall adsorbed concentration, s = 0
- (iv) The initial concentration of the solute c(x, y, z, t = 0) is uniform across the channel and has a Gaussian distribution along the channel.
- (v) The zeta potential for EOF does not vary over the bounding curve $\partial \Omega$ at a given axial location.

The following are the test problems we consider:

Case A: EOF with wall reaction and infinitely thin Debye Layers: The solute is transported by a uniform plug flow with adsorption and desorption on the walls. In Equation (4.23), the dimensionless equilibrium constant K will be held constant at the value 1 and λ will be varied to study the effect of varying wall reaction rates. This test problem can be related to separations by CEC [84] as well as the protein adsorption problem in CE [19]. The uniform flow profile corresponds to the following real life situations:

- (i) The solute is transported by electrophoresis alone in a channel where EOF has been suppressed.
- (ii) The channel width is much larger than the Debye length and the wall properties are uniform so that the EOF generated has a plug flow profile.

The Peclet number is 10 and numerical domain size in the x direction is L = 80b.

Case B: EOF with wall reaction and finite Debye Layers: Transport of a neutral solute in a channel with finite sized Debye layer will be analyzed, when an adsorption-desorption process (K = 1 and $\lambda K Pe = 1$) is present on the wall. The Debye layer thickness non-dimensionalized by the width of the channel will be varied.

4.4.2.2. Numerical Methods. The three-dimensional partial differential equation for c given by Equation (4.1) was solved in a rectangular box of size $2b \times 2b \times L$. At each time step, the boundary condition Equation (4.1a) was used to couple the c calculation from Equation (4.1b) to the s calculation from Equation (4.23). The s calculation used explicit Runge Kutta 4 (RK4) time stepping [85]. The unconditionally stable implicit time integration scheme (Crank Nicholson method) and spatial discretization, both of second order numerical accuracy [77] were used for solving the c field. The numerical grid size used was $\Delta x = \Delta y = \Delta z = 0.033$ for Cases A and B. The finite axial length L of the numerical domain was chosen large enough to satisfy $c(x = 0) = c(x = L) \leq 10^{-10}$ at all times. A zero total flux (diffusive+convective) boundary condition was applied at the ends of the channel. For solving the asymptotically reduced one-dimensional problem, RK4 time stepping and eighth order compact finite differences were used, similar to that in [31]. For calculating $\overline{\chi F}$

and $\overline{\Psi F}$ values tabulated in Table 4.5 for Case B, Gauss-Siedel iterations with successive [85] over-relaxation was used. A typical ratio of run times on a computer with CPU clock speed of 2 GHz and RAM of 512Mb computer for the one dimensional effective problem and the three dimensional problem was of the order of 10^{-2} . This considerable run-time economy is a considered a practical benefit of the asymptotically reduced model developed here in the modeling of microfluidic systems.

4.4.2.3. Metrics for Cases A and B. The speed of motion of the center of mass (CM) of the solute distribution will be called the migration speed. The migration speed $v_{\rm CM}$ and the effective dispersion coefficient D_{eff} defined below will be calculated from the numerical results will be used to study the migration and spreading of the solute plug under EOF.

(4.69a)
$$v_{\rm CM} = \frac{dx_{\rm CM}}{dt} = \frac{d}{dt} \left[\frac{\langle x\overline{c} \rangle}{\langle \overline{c} \rangle} \right]$$

(4.69b)
$$D_{eff} = \frac{1}{2} \frac{d\sigma^2}{dt} = \frac{d}{dt} \left[\frac{\langle (x - x_{\rm CM})^2 \overline{c} \rangle}{\langle \overline{c} \rangle} \right].$$

In the above $\langle ... \rangle$ indicates axial average. In general D_{eff} evaluated from Equation (4.69b) is a time dependent quantity. The figures presented will plot dimensional variables with their corresponding normalizing scales. The scale c_0 chosen for c is defined by $c_0 = 1/(2b)^3 \int c(x, y, z, t = 0) dV$ where dV is a volume element of the numerical solution domain.

4.4.2.4. Numerical Results for Case A. The problem to be studied in this application is a uniform flow with adsorption and desorption on the walls. In the wall reaction kinetics of Equation (4.23) K will be held constant at unity and λ will be varied to study the effect of varying reaction rates. The uniform flow represents an EOF when the channel width is much larger than the Debye layer thickness λ_D and the channel wall properties do not vary.



Figure 4.4: Loss of total concentration with time in purely pressure-driven flow in a cylindrical capillary for $Pe = \rho \overline{u}R/D = 10$ for different values of normalized adsorption rate constant βPe . The symbols denotes the result calculated by three-dimensional numerical solution and the solid line denotes the corresponding result from the asymptotic theory calculated from Equations (4.66) and (4.63b) applied to a cylindrical capillary.



Figure 4.5: The dependence of the rate constant B of the exponential decay of total quantity of solute on the normalized adsorption rate constant $\lambda K \text{Pe}$ for Pe = 5 and Pe = 10 in a cylindrical capillary calculated by three-dimensional numerical simulation (symbols) and estimated from asymptotic theory (solid line). The dependent variable is plotted on a logarithmic scale.



Figure 4.6: Speed of motion of the center of mass of the concentration distribution $(v_{\rm CM})$ in a purely pressure-driven flow in a cylindrical channel as a function of the normalized adsorption rate constant β Pe for Pe = 5 and Pe = 10. The symbols denotes the result calculated by three-dimensional numerical solution and the solid line denotes the corresponding result from asymptotic theory calculated using Equations (4.67) and (4.63c).



Figure 4.7: Normalized effective dispersion coefficient in a purely pressure-driven flow in a cylindrical channel as a function of the normalized adsorption rate constant β Pe for Pe = 10 (round symbols) and Pe = 5 (asterisks). The symbols denote the result calculated by three-dimensional numerical solution and the solid line denotes the corresponding result from asymptotic theory calculated using Equation (4.68).

For square channels $\alpha = 4$ and the uniform EOF implies $\chi = 0$ from Equation (4.10). The function Ψ can be obtained analytically by solving the 2-D boundary value problem in Equation (4.44) [76] and is shown in Table 4.2.

The theory of chromatography can be used to obtain a time independent analytical estimate of D_{eff} as follows. Choosing the dimensional speed of the plug as the velocity scale u_e , substituting $K' = \alpha K = 4$, Pe = 10, $\overline{u} = 1$ and $\overline{\Psi}_w = 1/24$, $\overline{\Psi}F = 0$ and $\overline{\chi}F = 0$ in Equation (4.42b), we get:

(4.70)
$$D_{eff, chrom} = \frac{11}{150} + \frac{4}{125\lambda}.$$

The estimate from the theory of chromatography (Equation (4.41)) for the center of mass speed is $v_{\rm CM} = 0.2$. The value of $\bar{\Psi}_w$, required in Equation (4.24), is found to be $\frac{1}{24}$ for square cross-section. For large λ , the approach to chemical equilibrium will be faster and the steady state migration speed and effective diffusion coefficient predicted by chromatography theory is expected to be applicable Equations (4.41) and (4.42) are expected to hold.

Figures 4.8 and 4.9 shows the evolution of migration speed and dispersion coefficient calculated by the simulation of the effective 1-D problem and the 3-D problem for three values of λ . The combination λK Pe mentioned in the figure caption indicates the ratio of the characteristic adsorption time to the characteristic width-wise diffusion time in the problem. The center of mass speed and dispersion coefficient pass through a transient phase that is well-represented by asymptotic theory before achieving values that are characteristic of the chromatographic quasi-equilibrium. Figure 4.4.2.4 shows the effect of λ on the dispersion coefficient predicted by the 1-D and 3-D simulations. The results from the theory of chromatography (Equation (4.70)) are also shown.

Figure 4.12 shows the solute distribution at $t\overline{u}/2b = 28$ for $\lambda K \text{Pe} = 1$ in the liquid phase \overline{c} (top pane) and solid phase \overline{s} (center pane) averaged at each cross-section of the channel. The predictions of the asymptotically reduced model (solid line) and the three-dimensional model are in good agreement. The \overline{c} distribution has a positive skewness. The bottom pane shows that the asymptotically reduced model can be used to calculate the solute distribution on cross-sectional planes, in good agreement with the three dimensional model.

Incidentally, 'fronted peaks' have been experimentally reported while performing capillary electrochromatography [30] and has been attributed to 'slow reactions' [30, 26] and have been predicted from the molecular kinetic theory of chromatography [29].

Figure 4.13 shows an interesting phenomenon in the transient phase for $\lambda K \text{Pe} = 1$, where a 'lump' in the \overline{c} distribution formed due to pile up of desorbed material (see, for example the distribution for $\frac{t\overline{u}}{2b} = 7.2$) grows progressively in mass to overwhelm the erstwhile primary peak upstream at a time between $\frac{t\overline{u}}{2b} = 8.4$ and $\frac{t\overline{u}}{2b} = 8.6$. Before this event the \overline{c} distribution is tailed (negative skewness) and after this event the distribution is fronted (positive skewness). The inset shows this effect on the peak motion. The jump corresponding to the formation of the new peak is accurately resolved by the asymptotically reduced model. **4.4.2.5. Numerical Results for Case B.** The flow profile F_{κ} in a rectangular channel of width $w_0 = 2b$ and height 2c can be calculated from Equation (4.55a). The electric potential distribution Φ required in this equation can be obtained analytically from Equation (4.55b) and Equation (4.55c). We choose $w_0 = 2b$ and Figure 3.1 for our coordinate system. Then the dimensionless Debye Hückel parameter is $\kappa' = \frac{2b}{\lambda}$. Defining r = b/c, we get, based on the solution by method of separation of variables in [86]:

(4.71)
$$\phi = 4 \left[\sum_{n=0}^{\infty} (-1)^n \left\{ \frac{\cos\left[(2n+1)\pi y\right] \cosh\left[\alpha_n z\right]}{(2n+1)\pi \cosh\left[\frac{\alpha_n}{2r}\right]} + \frac{\cosh\left[(2n+1)\pi zr\right] \cos\left[\mu_n y\right]}{(2n+1)\pi \cosh\left[\frac{\mu_n r}{2}\right]} \right\} \right]$$

where $\alpha_n = \sqrt{\mathcal{K}^2 + \{(2n+1)\pi\}^2}$ and $\mu_n = \sqrt{\mathcal{K}^2 + \{(2n+1)\pi r\}^2}$. A reduction in crosssectional area of the channel leads to increasingly inhomogeneous flow and a reduction in the volume flow rate in a channel due to finite Debye layer effects. However, the effect of flow inhomogeneity alone can be isolated experimentally, by readjusting the electric field strength upwards to get the same flow rate. Parameterizing F_{κ} with κ' can be interpreted to represent this situation.

We consider a square channel (r = 1) for numerical comparison. In addition to the flow with finite Debye layers, there is a linear absorption-desorption process on its wall characterized by the desorption coefficient $\lambda = 0.1$ and equilibrium constant K = 1 and represented by Equation (4.23). From Table 4.2, the coefficient $\overline{\Psi}_w = \frac{1}{24}$. The coefficients $\overline{\chi_{\kappa}F_{\kappa}}$ and $\overline{\chi}_w$ has been calculated numerically using Equation (4.10),(4.55a) and (4.71). The values of these two coefficients for various values of κ' are tabulated in Table 4.5.

The migration speed of the center of mass is expected to have a dependence on only the equilibrium constant K, if sufficient time is allowed to the adsorption-desorption process to come to a quasi-equilibrium. In the event the reaction speed is not so large as to achieve this quasi-equilibrium within the time of analysis, the asymptotic theory can be used to predict the migration speed, as shown in Figure 4.14. T Close to the wall, there is a zone of low-speed streamlines from which solute particles can be trapped easily by the wall, streamlines with higher speed make solutes more prone to stay in the liquid phase. The zone of low-speed streamlines is larger for flows with larger Debye layers; resulting in slower overall motion of

$\kappa' = \frac{2b}{\lambda_D}$	$-\overline{\chi_{\kappa}F_{\kappa}}$	$-\overline{\psi F_{\kappa}}$
4	0.0067	0.0140
8	0.0042	0.0115
12	0.0026	0.00932
16	0.0017	0.00772
20	0.0012	0.00655
24	0.0009	0.00568
28	0.00067	0.00500
32	0.00053	0.00447
36	0.00043	0.00403

Table 4.5: Dependence of the coefficients $\overline{\chi_{\kappa}F_{\kappa}}$ and $\overline{\psi}F_{\kappa}$ on Debye Hückel parameter $\kappa = \frac{2b}{\lambda_D}$ in Case B.

the plug in nanochannels with large Debye lengths. This accounts for a minor decrease of migration velocity with increasing Debye length (decreasing κ'). The migration speeds are calculated at time $t\overline{u}/2b = 7.75$.

Owing to the Taylor-Aris dispersion mechanism, the decrease of κ' should lead to higher effective dispersion coefficient. The effect of decreasing κ' on the effective dispersion coefficient at time $t\overline{u}/2b = 7.75$, calculated with the 1-D model and 3-D model are shown in Figure 4.15. In both figures, predictions from the 1-D model are in good agreement with the 3-D results.



Figure 4.8: Migration speed $v_{\rm CM}$ vs. time (t) for $\lambda K {\rm Pe} = 1, 3, 5, 10$ in Case A. Solid lines indicate results from 3-D numerical simulation and dashed lines indicate results from simulation of the 1-D model.



Figure 4.9: Effective Dispersion Coefficient D_{eff} vs. time (t) for $\lambda KPe = 1, 3, 5, 10$ in Case A. Dashed lines indicate results from three dimensional numerical simulation and solid lines indicate results from simulation of the asymptotically reduced model.



Figure 4.10: Migration speed $v_{\rm CM}$ at time $\frac{t\overline{u}}{2b} = 8$ vs. adsorption rate constant (λK Pe) in Case A. Results from 3-D numerical simulation are indicated by asterisks and results from simulation of the 1-D model is indicated by circles. The solid line is the result calculated from the theory of chromatography ($\frac{v_{\rm CM}}{\overline{u}} = \frac{1}{1+\alpha K}$). Here, $\alpha = 4$ and K = 1.



Figure 4.11: Effective dispersion coefficient (D_{eff}) at time $\frac{t\overline{u}}{2b} = 8$ vs. adsorption rate constant $(\lambda K \text{Pe})$ in Case A. Results from 3-D numerical simulation are indicated by asterisks and results from the asymptotically reduced model is indicated by circles. The solid line is the result calculated from the theory of chromatography (Equation (4.70)).



Figure 4.12: The top pane shows cross-sectionally averaged concentration (\bar{c}) at time $\frac{t\bar{u}}{2b} = 28$ calculated for Case A by the three-dimensional model (dotted line) and asymptotically reduced model (solid line). The center pane shows the perimetrically averaged adsorbed concentration distribution at the same time calculated by the three-dimensional model (dotted line) and asymptotically reduced model (solid line). In the top and bottom panes the \bar{c} and \bar{s} values at cross-sectional planes at x/2b = 8.33, 15, 20 are represented by the symbols $\nabla, +, *$ respectively. In the bottom pane, the concentration distributions on the line z = 0 at time $\frac{t\bar{u}}{2b} = 28$ is shown for the three marked planes, as calculated by the three-dimensional model (symbols $\nabla, +, *$) and the asymptotically reduced model (solid line). Here, K = 1 and $\lambda K \text{Pe} = 1$.



Figure 4.13: Formation of a secondary peak in Case A for K = 1 and $\lambda K Pe = 1$ shown by plotting concentration distributions at times $\frac{t\bar{u}}{2b} = 7.2, 8, 8.4, 8.8, 9.6$. The dotted lines represent results from the three-dimensional model and the solid lines represent results from the asymptotically reduced model. The inset shows the variation in position of the solute concentration peak (x_{peak}) with time. In the inset, circular symbols represent results from three dimensional solution and the solid line represents results from three dimensional solution and the solid line represents results from the simulation of the asymptotic model.



Figure 4.14: Effect of the Dimensionless Debye-Hückel Parameter $(\kappa' = \frac{2b}{\lambda_D})$ on the migration velocity $v_{\rm CM}$ at time $t\overline{u}/2b = 7.75$ calculated from 3-D numerical simulation (asterisks) and simulation of 1-D model (circles).



Figure 4.15: Effect of the Dimensionless Debye-Hückel Parameter $(\kappa' = \frac{2b}{\lambda_D})$ on the effective dispersion coefficient D_{eff} at time $t\overline{u}/2b = 7.75$ in Case B calculated from 3-D numerical simulation (asterisks) and simulation of 1-D model (circles).

4.5. Summary

In Section 4.1, we have asymptotically reduced the three-dimensional problem for the transport of a solute in an uniform channel of arbitrary cross-sectional shape with arbitrary kinetics of adsorption and desorption on the wall. Equations (4.18) and (4.20) represent the main outcome of the asymptotic reduction.

In Section 4.2, we have specified the wall reaction kinetic function, specialized it to linear kinetics and further treated the limit where adsorption and desorption speeds are much larger than the axial transit speed. This limit is central to the study of zone migration and band broadening in adsorption chromatography and our model furnishes purely analytical results in agreement with the literature on adsorption chromatography in this limit.

Cross-sectional shapes like the circle, gap between parallel plates, rectangle and trapezoids and flow patterns like pressure-driven, electrokinetic and wall-shear-driven differ merely in the calculation of some shape functions and their statistics in our approach. The method of treating various cross-sections, adsorption patterns and flow types in our reduced numerical model as well as the analytical results for chromatography have been discussed with examples in the Section 4.3.

In Section 4.4, we have solved the complete transport problem numerically, for purposes of comparison with results from our asymptotically reduced model. An irreversible adsorption in cylindrical geometry, a uniform flow in a rectangular channel with wall adsorptiondesorption and a finite Debye-layer electroosmotic flow with wall adsorption-desorption have been studied as test cases. The results from the asymptotically reduced model compare favorably with the results from the direct numerical solution.

CHAPTER 5

Dispersion in the Presence of Wall Interactions in the Presence of Axial Inhomogeneity

5.1. Introduction

The problem of transport of a solute in axially variable flows can be motivated by applications to microfluidic chemical analysis techniques such as capillary electrophoresis (CE) and open-channel capillary electrochromatography (CEC) [6, 87]. Both the techniques employ electro-osmotic flow (EOF) to transport the solute and the buffer and are often performed with the same experimental instrumentation. However, in CEC, the interaction of a solute with a coating bonded to the channel wall serves as the separation principle [27, 72]; in CE wall interaction is often an undesirable effect [20, 23, 31]. Apart from end effects, an 'ideal EOF' does not have axial variation. However, any axial variation in the zeta potential (as discussed in Section (2.6)) or cross-sectional geometry results in flow inhomogeneities, which in turn lead to enhanced solute dispersion by the Taylor-Aris dispersion mechanism [9, 10]. In this chapter, the general problem of transport under axially variable flow and geometry will be studied in the long time limit. Applications employing electroosmotic flow will then be discussed. The 1-D model developed from the analysis will be compared with 3-D numerical solution in case of solute transport in an electroosmotic flow arising from zeta potential variation on the walls of a rectangular channel.



Figure 5.1: Geometry of the axially variable channel

5.2. Dispersion in Slowly Varying Channels

Consider a straight channel with arbitrarily varying cross-section and wall charge (Figure 5.1) in which there is an incompressible flow $\mathbf{u}(x, y, z, t)$, where x, y, z are the coordinates of an orthogonal co-ordinate system with the x-axis along the axis of the channel. At any point on the wall of the channel, the surface normal is given by $\hat{\mathbf{n}}$. The channel carries a solute of concentration c(x, y, z, t) moles per unit area, some of which is adsorbed to the wall, which has a wall concentration s(x, y, t) moles per unit area. We choose a characteristic channel width w_0 as our unit of length and w_0/u_e as our unit of time where u_e is a characteristic flow speed. We assume that the concentration c has been normalized by some characteristic value c^* and the wall concentration s by c^*w_0 . The Peclet number is $\text{Pe} = (u_e w_0)/D$, where D is the diffusivity. Then the following equations describe the time evolution of the c(x, y, z, t):

(5.1a)
$$\frac{\partial c}{\partial t} + \mathbf{u}\nabla c = \mathrm{Pe}^{-1}\nabla^2 c$$

(5.1b)
$$\operatorname{Pe}^{-1} \nabla c \cdot \hat{\mathbf{n}} = -\frac{\partial s}{\partial t}$$
 on wall.

As shown in Figure 5.1, the cross-section of the channel at each axial location x is denoted by the planar region $\Omega(x)$ bounded by the curve $\partial \Omega(x)$. The normal to $\partial \Omega$ is $\hat{\mathbf{n}}_{\Omega}$.

We suppose that a time much larger than the diffusion time across the channel (i.e. $t \gg \text{Pe}$) has elapsed so that any axial variation takes place on a long length scale and a slow time scale. We define the scaled 'slow variables' $X = \epsilon x$ and $T = \epsilon t$. In order to ensure slow variation, any dependence of the flow u(x, y, z, t) on x and t has to be slow and the cross-section of the capillary should change slowly in the axial direction. The latter requirement means the surface normal $\hat{\mathbf{n}}$ at any point on the wall makes a small angle with the x- axis,

or in other words:

(5.2)
$$\hat{\mathbf{n}} = \epsilon l \hat{\mathbf{x}} + \sqrt{1 - \epsilon^2 l^2} \hat{\mathbf{n}}_{\Omega}$$

where $\hat{\mathbf{n}}_{\Omega}$ is the unit normal at the boundary $\partial \Omega(X)$ of the 2D domain $\Omega(x)$. If the axial velocity u is O(1) from the requirements of continuity of flow, the cross-flow velocity components v and w must be $O(\epsilon)$. So, we write: $\mathbf{u} = U\hat{\mathbf{x}} + v\hat{\mathbf{y}} + w\hat{\mathbf{z}} = U\hat{\mathbf{x}} + \epsilon \mathbf{U}_{\perp}$ and construct the following asymptotic expansion for the velocity field:

(5.3a)
$$u = U(X, Y, Z, T; \epsilon) = U^{(0)} + \epsilon U^{(1)} + \cdots$$

(5.3b)
$$v\hat{\mathbf{y}} + w\hat{\mathbf{z}} = \epsilon \mathbf{U}_{\perp} = \epsilon \mathbf{U}_{\perp}^{(0)} + \epsilon^2 \mathbf{U}_{\perp}^{(1)} + \cdots$$

Changing variables x and t to X and T, Equation (5.1) becomes:

(5.4a)
$$\epsilon \frac{\partial c}{\partial T} + \epsilon U \frac{\partial c}{\partial X} + \epsilon \mathbf{U}_{\perp} \cdot \nabla_{\Omega} c - \epsilon^2 \mathrm{Pe}^{-1} \frac{\partial^2 c}{\partial X^2} = \mathrm{Pe}^{-1} \nabla_{\Omega}^2 c$$

(5.4b)
$$\operatorname{Pe}^{-1}\left\{ \left. \sqrt{1 - \epsilon^2 l^2} \nabla_{\Omega} c \cdot \hat{\mathbf{n}}_{\Omega} + \epsilon^2 l \frac{\partial c}{\partial X} \right|_{\partial \Omega} \right\} = -\epsilon \frac{\partial s}{\partial T}.$$

The variables c and s can be expanded in powers of ϵ :

(5.5a)
$$c = c^{(0)} + \epsilon c^{(1)} + \cdots$$

(5.5b)
$$s = s^{(0)} + \epsilon c^{(1)} + \cdots$$

and substituted in Equations (5.4a) and (5.4b). Then at O(1) we have:

(5.6a)
$$\operatorname{Pe}^{-1} \nabla_{\Omega}^{2} c^{(0)} = 0$$

(5.6b)
$$-\operatorname{Pe}^{-1}\nabla_{\Omega}c^{(0)}\cdot\hat{\mathbf{n}}_{\Omega}\big|_{\partial\Omega}=0.$$

This implies that $c^{(0)}$ is independent of the cross-sectional coordinates y and z, that is $c^{(0)} = \overline{c}^{(0)}(X,T)$. A bar over a quantity indicates an average defined at each axial location X and time T, the quantities defined inside the channel (e.g. c) are averaged over the cross-sectional region $\Omega(X)$, quantities defined on the wall of the channel (e.g. s) are averaged over the boundary curve $\partial \Omega(X)$.

At $O(\epsilon)$ we have:

(5.7a)
$$\operatorname{Pe}^{-1}\nabla_{\Omega}^{2}c^{(1)} = \frac{\partial \overline{c}^{(0)}}{\partial T} + U^{(0)}\frac{\partial \overline{c}^{(0)}}{\partial X}$$

(5.7b)
$$-\operatorname{Pe}^{-1}\nabla_{\Omega}c^{(1)}\cdot\hat{\mathbf{n}}_{\Omega}\big|_{\partial\Omega} = \frac{\partial s^{(0)}}{\partial T}$$

Equation (5.7) and (5.7b) have no solutions unless a solvability condition is satisfied by the lower order solution. This can be found by integrating either sides of Equation (5.7a) in the region $\Omega(X)$, using the two-dimensional Gauss Divergence Theorem and Equation (5.7b) to convert area integrals on $\Omega(X)$ to line integrals on $\partial\Omega(X)$. We define $\alpha(X)$ as the ratio of the perimeter (Γ) and area (A) of the cross-section at any X. Then:

(5.8)
$$\frac{\partial \overline{c}^{(0)}}{\partial T} + \overline{U}^{(0)} \frac{\partial \overline{c}^{(0)}}{\partial X} = -\alpha \frac{\partial \overline{s}^{(0)}}{\partial T}$$

Equation (5.8) can be used to rewrite Equation (5.7) as follows:

(5.9a)
$$\operatorname{Pe}^{-1} \nabla_{\Omega}^{2} c^{(1)} = -\alpha \frac{\partial \overline{s}^{(0)}}{\partial T} + (U^{(0)} - \overline{U}^{(0)}) \frac{\partial \overline{c}^{(0)}}{\partial X}$$

(5.9b)
$$-\operatorname{Pe}^{-1}\nabla_{\Omega}c^{(1)}\cdot\hat{\mathbf{n}}_{\Omega}\Big|_{\partial\Omega} = \frac{\partial s^{(0)}}{\partial T}.$$

Equation (5.9) has solutions of the form:

(5.10)
$$c^{(1)} = \overline{c}^{(1)} + \operatorname{Pe}\left[-\alpha \frac{\partial \overline{s}^{(0)}}{\partial T} \Psi^{(0)}(x, y, z) + \overline{U}^{(0)} \frac{\partial \overline{c}^{(0)}}{\partial X} \chi^{(0)}(x, y, z)\right].$$

Here, $\Psi^{(0)}$ is defined by the following boundary value problem:

(5.11a)
$$\nabla_{\Omega}^{2} \Psi^{(0)} = 1$$

(5.11b)
$$\nabla_{\Omega} \Psi^{(0)} \cdot \hat{\mathbf{n}}_{\Omega} = \frac{1}{\alpha} \frac{\partial s^{(0)}}{\partial T} / \frac{\partial \overline{s}^{(0)}}{\partial T}$$

$$\overline{\Psi^{(0)}} = 0.$$

Equation (5.11c) is imposed in order to eliminate the arbitrariness of $\Psi^{(0)}$ up to a constant. Similarly, $\chi^{(0)}$ is defined by the boundary value problem:

(5.12a)
$$\nabla_{\Omega}^{2} \chi^{(0)} = \frac{U^{(0)}}{\overline{U}^{(0)}} - 1$$

(5.12b)
$$\nabla_{\Omega} \chi^{(0)} \cdot \hat{\mathbf{n}}_{\Omega} \mid_{\partial \Omega} = 0$$

(5.12c)
$$\overline{\chi^{(0)}} = 0.$$

At order $O(\epsilon^2)$ we have:

(5.13a)
$$\operatorname{Pe}^{-1}\nabla_{\Omega}^{2}c^{(2)} = \frac{\partial c^{(1)}}{\partial T} + U^{(0)}\frac{\partial c^{(1)}}{\partial T} + U^{(1)}\frac{\partial \overline{c}^{(0)}}{\partial X} + \mathbf{U}_{\perp}^{(\mathbf{0})} \cdot \nabla_{\Omega}c^{(1)} - \operatorname{Pe}^{-1}\frac{\partial^{2}\overline{c}^{(0)}}{\partial X^{2}}$$

(5.13b)
$$-\operatorname{Pe}^{-1}\nabla_{\Omega}c^{(2)}\cdot\hat{\mathbf{n}}_{\Omega}\Big|_{\partial\Omega} = \frac{\partial s^{(1)}}{\partial T} + \operatorname{Pe}^{-1}l\frac{\partial \overline{c}^{(0)}}{\partial X}.$$

Integration of both sides of Equation (5.13a) over the region $\Omega(X)$ and use of Equation (5.13b) yields:

$$-\frac{\partial \overline{s}^{(1)}}{\partial T}\Gamma = -\operatorname{Pe}^{-1}\left(A\frac{\partial^{2}\overline{c}^{(0)}}{\partial X^{2}} - \frac{\partial \overline{c}^{(0)}}{\partial X}\oint_{\partial\Omega}ld\underline{s}\right) + \left(\int_{\Omega}U^{(0)}\frac{\partial c^{(1)}}{\partial X}dA + \int_{\Omega}\mathbf{U}_{\perp}^{(0)}\cdot\nabla_{\Omega}c^{(1)}dA\right)$$

$$(5.14) \qquad +A\bar{u}_{1}\frac{\partial \overline{c}^{(0)}}{\partial X} + A\frac{\partial \overline{c}^{(1)}}{\partial T}$$

where A has already been defined as the area of the region $\Omega(X)$. The terms enclosed in brackets in Equation (5.14) can be simplified using the following geometrical result derived in Appendix A:

(5.15)
$$\frac{\partial \left(\int_{\Omega} F dA\right)}{\partial X} = \int_{\Omega} \frac{\partial F}{\partial X} dA - \oint_{\partial \Omega} F ld\underline{s},$$

the continuity of fluid:

(5.16)
$$\frac{\partial U}{\partial X} + \nabla \cdot \mathbf{U}_{\perp} = 0$$

and the fact that the fluid cannot penetrate the channel walls:

$$\mathbf{u} \cdot n = 0$$

In Equation (5.15), F(y, z) is a continuous and differentiable function of y, z.

The terms enclosed in brackets in Equation (5.14) become:

(5.18a)
$$A\frac{\partial^2 \overline{c}^{(0)}}{\partial X^2} - \frac{\partial \overline{c}^{(0)}}{\partial X} \oint_{\partial \Omega} l d\underline{s} = \left(A\frac{\partial \overline{c}^{(0)}}{\partial X}\right)_X$$

(5.18b)
$$\int_{\Omega} U^{(0)} \frac{\partial c^{(1)}}{\partial X} dA + \int_{\Omega} \mathbf{U}_{\perp}^{(0)} \cdot \nabla_{\Omega} c^{(1)} dA = \left(A \, \overline{c^{(1)} U^{(0)}} \right)_{X}.$$

Substituting this in Equation (5.14) we get the following solvability condition for the problem at $O(\epsilon^2)$:

(5.19)
$$-\alpha A \frac{\partial \overline{s}^{(1)}}{\partial T} = -\operatorname{Pe}^{-1} \frac{\partial}{\partial X} \left(A \frac{\partial \overline{c}^{(0)}}{\partial X} \right) + \frac{\partial}{\partial X} \left(A \overline{c^{(1)}U^{(0)}} \right) + A \overline{u}_1 \frac{\partial \overline{c}^{(0)}}{\partial X} + A \frac{\partial \overline{c}^{(1)}}{\partial T}.$$

We can obtain a single equation for $c = c^{(0)} + \epsilon c^{(1)} + O(\epsilon^2)$ by combining Equations (5.8) and (5.19). Adding A times Equation (5.8),with ϵ times Equation (5.19) and the terms $\epsilon^2 (A \, \overline{c^{(1)}U^{(1)}})_X$ and $-\epsilon^2 \text{Pe}^{-1} \left(A \frac{\partial \overline{c}^{(1)}}{\partial X} \right)_X$ which do not affect the asymptotic validity of the resultant equation and reverting to independent variables $t = T/\epsilon$ and $x = X/\epsilon$:

(5.20)
$$-\alpha A \frac{\partial \overline{s}}{\partial t} = -\operatorname{Pe}^{-1} \frac{\partial}{\partial x} \left(A \frac{\partial \overline{c}}{\partial x} \right) + \frac{\partial}{\partial x} (A \overline{cu}) + A \frac{\partial \overline{c}}{\partial t}.$$

In the above, $\frac{\partial(\overline{U}A)}{\partial x} = 0$ has been used to obtain the term $\frac{\partial(A \overline{cu})}{\partial x}$. Combining $c^{(0)} = \overline{c}^{(0)}$ and Equation (5.10) and reverting to t and x:

(5.21)
$$c = \overline{c} + \operatorname{Pe}\left[-\alpha \frac{\partial \overline{s}}{\partial t}\Psi(x, y, z) + \overline{u} \frac{\partial \overline{c}}{\partial x}\chi(x, y, z)\right]$$

where $\Psi = \Psi^{(0)} + O(\epsilon)$ and $\chi = \chi^{(0)} + O(\epsilon)$ are calculated by modifying the boundary value problems in Equations (5.11) and (5.12):

(5.22a)
$$\nabla_{\Omega}^{2}\Psi = 1$$

(5.22b)
$$\nabla_{\Omega}\Psi \cdot \hat{\mathbf{n}}_{\Omega} = \frac{1}{\alpha} \frac{\partial s}{\partial T} / \frac{\partial \overline{s}}{\partial T}$$

$$(5.22c) \qquad \qquad \overline{\Psi} = 0$$

(5.23a)
$$\nabla_{\Omega}^{2}\chi = \frac{u}{\overline{u}} - 1$$

(5.23b)
$$\nabla_{\Omega} \chi \cdot \hat{\mathbf{n}}_{\Omega} \mid_{\partial \Omega} = 0$$

(5.23c)
$$\overline{\chi} = 0.$$
Equation (5.21) can be substituted in Equation (5.20). Defining the coefficients β and γ by :

(5.24a)
$$\beta \overline{u} = -\overline{\Psi u}$$

(5.24b)
$$\gamma \overline{u} = -\overline{\chi u}$$

we get:

(5.25a)
$$A\frac{\partial \overline{c}}{\partial t} + \frac{\partial}{\partial x}(A\overline{u}\overline{c}) = -\alpha A\frac{\partial \overline{s}}{\partial t} + \frac{\partial}{\partial x}\left(AD^*\frac{\partial \overline{c}}{\partial x}\right) - \operatorname{Pe}\frac{\partial}{\partial x}\left(\alpha A\beta \overline{u}\frac{\partial \overline{s}}{\partial t}\right)$$

$$(5.25b) D^* = \mathrm{Pe}^{-1} + \gamma \mathrm{Pe}\overline{u}^2.$$

Equation (5.25) and Equation (5.25) and (5.21) are our asymptotic equations for determining c.

5.3. Dispersion in an Inhomogeneous Electroosmotic Flow

Microfluidic separations often employ electroosmotic flow, which is rendered axially variable in various circumstances [17, 6]. Motivated by these applications, we will consider an electroosmotic flow in a channel of constant cross-section, when the wall zeta potential can vary over the wall. We assume that the characteristic scale of axial variation in ζ is much larger than the characteristic channel width and the Reynolds number of the resultant electroosmotic flow to be zero. The lubrication theory of [15] can be used to obtain the following expression for axial velocity distribution for correct up to $O(\epsilon^2)$:

(5.26a)
$$\overline{u} = \frac{\overline{\mathcal{P}}(P_a - P_b)}{L} + \langle \overline{\mathcal{E}} \rangle$$

(5.26b)
$$u = \overline{u} \left[1 + \left(\frac{\mathcal{P}}{\overline{\mathcal{P}}} - 1\right) \left(1 - \frac{\overline{\mathcal{E}}}{\overline{u}}\right) + \left(\frac{\mathcal{E}}{\overline{\mathcal{E}}} - 1\right) \frac{\overline{\mathcal{E}}}{\overline{u}} \right].$$

The function \mathcal{E} has been defined by Equation (4.50) in the last chapter and can be used to generate the pressure-driven flow profile $F_p = \frac{\mathcal{P}}{\mathcal{P}}$. The functions \mathcal{E} has been defined by Equation (4.57) in the last chapter and can be used to generate the profile $F_s = \frac{\mathcal{E}}{\mathcal{E}}$ representing the effect of variation of zeta potential over the boundary at a given cross-section, or boundary shear. The function χ and axially variable factors $\overline{\chi}_w, \beta, \gamma$ for electroosmotic flow can be calculated from the corresponding functions and coefficients for F_p and shear flow F_s . Examples of calculating these quantities for flow shapes F_p and F_s in various cross-sectional geometries have been covered in the last chapter and appear in Table 4.1 for F_p and Table 4.3 for F_s . Using Equation (5.26) in Equations (5.24a) and (5.24b):

(5.27a)
$$\chi \overline{u} = (\overline{u} - \overline{\mathcal{E}})\chi_{pw} + \overline{\mathcal{E}}\chi_{sw}$$

(5.27b)
$$\beta \overline{u} = -\left[\overline{\psi F_p}(\overline{u} - \overline{\mathcal{E}}) + \overline{\psi F_s}\overline{\mathcal{E}}\right]$$

(5.27c)
$$\gamma \overline{u}^2 = -\left[\overline{\chi_p F_p} (\overline{u} - \overline{\mathcal{E}})^2 + 2 \overline{\chi_s F_p} \overline{\mathcal{E}} (\overline{u} - \overline{\mathcal{E}}) + \overline{\chi_s F_s} \overline{\mathcal{E}}^2\right]$$

where the relationship:

(5.28)
$$\overline{\chi_p F_s} = \overline{\chi_s F_p}$$

derived in Appendix B has been used to remove the appearance of $\overline{\chi}_w$.

In the applications to be considered in this chapter, $\frac{\partial \overline{s}}{\partial t} = \frac{\partial s}{\partial t} + O(\epsilon)$ will be valid ,leading the right hand side of Equation (5.22b) to equal 1. We can also conclude $\overline{\chi}_w = \beta$ from the derivation in Appendix B.

5.3.1. Dispersion under an Axial Distribution of Zeta Potential in Absence of Adsorption-desorption

We consider transport under an electroosmotic flow with the zeta potential $\mathcal{Z}(x)$ varying only in the axial coordinate and with no adsorption-desorption $(\frac{\partial s}{\partial t} = 0)$ on its walls. Then, the problem Equation (4.57), has a solution $\mathcal{E} = \mathcal{Z}$; so we get $\bar{\mathcal{E}} = \mathcal{Z}$. Equations (5.26), (5.27a) and (5.27c) specialize to:

(5.29a)
$$\overline{u} = \langle \mathcal{Z} \rangle$$

(5.29b)
$$u = \overline{u} \left[1 + \left(1 - \frac{\mathcal{Z}}{\langle \mathcal{Z} \rangle} \right) (F_p - 1) \right]$$

(5.30a)
$$\chi \overline{u} = (\langle \mathcal{Z} \rangle - \mathcal{Z}) \chi_{pw}$$

(5.30b)
$$\gamma \overline{u}^2 = -\overline{\chi_p F_p} (\langle \mathcal{Z} \rangle - \mathcal{Z})^2.$$

Substituting the above relations in (5.25):

(5.31)
$$\frac{\partial \bar{c}}{\partial t} + \bar{u}\frac{\partial \bar{c}}{\partial x} = \frac{\partial}{\partial x}\left(D^*\frac{\partial \bar{c}}{\partial x}\right)$$

where the effective dispersion coefficient is:

(5.32)
$$D^* = \frac{1}{\text{Pe}} + \gamma_p \operatorname{Pe} u_{pr}^2$$

Here, $u_{pr} = \langle \mathcal{Z} \rangle - \mathcal{Z}$ can be interpreted as the pressure driven part of the mean electroosmotic flow $\overline{u} = \langle \zeta \rangle$. This equation indicates that the molecular diffusion is reinforced by Taylor-Aris dispersion due to $u_{pr} = \langle \mathcal{Z} \rangle - \mathcal{Z}$, the part of the mean flow \overline{u} contributed by the induced pressure distribution. The coefficient $\gamma_p = -\overline{\chi_p F_p}$ depends on the cross-sectional geometry (Table 4.2).

5.4. Numerical Comparisons

5.4.1. The Test Problem

In order to ascertain the accuracy of the asymptotic reduction in case of inhomogeneous flow distributions, we will numerically simulate the transport of a solute under three-dimensional inhomogeneous electroosmotic flow in a channel whose cross-section is a square of side $w_0 = 2b$. The \mathcal{Z} distribution on each side wall of the square channel is prescribed to be:

(5.33)
$$\mathcal{Z} = \zeta_0 + \Delta \zeta \cos(2\pi x/\lambda)$$

where $\Delta \zeta$ and λ are parameters that will be varied to change the shape of the \mathcal{Z} waveform in the simulations. The Reynolds number of the flow is zero and the Peclet number calculated with $w_0 = 2b$ of the dispersing solute is 5. Referring to Table 4.2, the value of $\gamma_p = -\overline{\chi_p F_p}$ to be used in Equation (5.32) is 0.0084.

Next, the solute distribution and effective dispersion coefficient in this problem will be calculated by the following two methods:

- (i) solving the asymptotically reduced model numerically. This involves a time-dependent one-dimensional numerical solution of Equation (5.31).
- (ii) by solving Equation (5.1) in three dimensions.

The corresponding results will be parameterized by the wavelength λ and amplitude $\Delta \zeta$ of the \mathcal{Z} waveform. Since the 1-D theoretical model is derived with lubrication approximation [15] for the flow and the long time limit [31] for transport, it is expected to represent the 3-D problem more accurately for large λ and small $\Delta \zeta$.

5.4.2. Numerical Methods

The electroosmotic flow field was calculated using the numerical methods described in Section 3.3. However, preliminary numerical experiments and the need to investigate longer elapsed times that allow the solute peaks to be wider than the half-waves of applied zeta potential lead to the choice of a larger numerical domain size L = 256b. The numerical grid size was $1.5\Delta x = \Delta y = \Delta z = 0.04$. The methods for the three-dimensional solution the solute concentration distribution under this flow field are identical to that described in Section 4.4.2.2.

5.4.3. Numerical Results

The variation of the effective dispersion coefficient with time is plotted for the wavelengths $\Lambda = L/5 = 51.2b$, $\Lambda = L/10 = 25.6b$ and $\Lambda = L/25 = 10.24b$ in the three panes of Figure 5.2, when the amplitude $\zeta = 0.75\zeta_0$ is fixed. The predictions of the asymptotically reduced model for the wavelengths $\Lambda = L/5 = 51.2b$ and $\Lambda = L/10 = 25.6b$ are reasonably accurate. For $\lambda = L/25 = 10.24b$, some inaccuracies are visible. This is because the assumption of slow spatial variation used for the asymptotic reduction of the concentration field and the

lubrication approximation of the flow field [15] is inappropriate for short wavelength perturbations. If the elapsed time is long enough for the characteristic width of the \bar{c} distribution to significantly exceed than the half wave of wall zeta potential perturbation, the effective dispersion coefficient achieves a stationary value, as in the center and bottom panes. The three dimensional solution for $\lambda = L/10$ and $\Lambda = L/25$ in Figure 5.2 show a short transient period corresponding to cross-diffusion, for which asymptotic results are inaccurate.

The effect of varying $\Delta \zeta$ on D_{eff} is shown in Figure 5.3. A higher perturbation in the electroosmotic flow produces higher dispersion, since $\gamma \overline{u}^2 = 0.0084 (\langle \zeta \rangle - \zeta)^2$. The predictions of the asymptotically reduced model are in good agreement with the threedimensional results.

Figure 5.4 shows that the area averaged concentration distribution for one-dimensional model is a reasonably accurate approximation for three-dimensional numerical results for dimensionless elapsed times greater than or equal to t = 5 or tPe = 1, when $\Lambda = L/5 = 51.2b$ and $\Delta \zeta/\zeta_0 = 0.75$.



Figure 5.2: Effective dispersion coefficient (D_{eff}) vs. time (t) for axially variable zeta potential of wavelength Λ calculated from three dimensional numerical simulation (solid line) and simulation of one dimensional model (circular symbols) are shown in top, center and bottom panes for $\Lambda = L/5 = 51.2b$, $\Lambda = L/10 = 25.6b$ and $\Lambda = L/25 = 10.24b$ respectively. Here, $\Delta \zeta = 0.75 \zeta$.



Figure 5.3: Effective dispersion coefficient (D_{eff}) vs. time (t) for axially variable zeta potential with three different wave amplitude values $\Delta \zeta/\zeta = 0.75, 2.5, 3.5$ are shown in the top, center and bottom panes calculated from three dimensional numerical simulation (circular symbols) and simulation of one dimensional model (solid line) are shown in Panes A-C. Here, $\Lambda = L/5 = 51.2b$ respectively.



Figure 5.4: Concentration distribution from full three-dimensional numerical solution (symbols) and solution of the one-dimensional model (solid lines) for $\Delta\zeta/\zeta_0 = 0.75$ and $\lambda = L/5 = 51.2b$ at $\frac{t\overline{u}}{2b} = 0, 5, 10, 15, 20, 25, 30, 35, 40, 45$.



Figure 5.5: An applied zeta potential distribution of wave length $\Lambda = L/5 = 51.2b$ and amplitude $\Delta \zeta/\zeta = 0.75$ is shown in the top pane and the symbols ∇ , + and * mark the zeta potential values at three cross-sectional planes at x/2b = 71.5, 77.5, 82 respectively. The center pane shows the resultant cross-sectionally averaged concentration distribution calculated at time $\frac{t\overline{u}}{2b} = 15$ with asymptotically reduced model (solid line) and three-dimensional model (dotted line). The same symbols as in the top pane are used to mark the average concentration values at x/2b = 71.5, 77.5, 82. The bottom pane shows concentration distributions on the line z = 0 at the planes located at x/2b = 71.5, 77.5, 82 calculated from three-dimensional simulation (symbols ∇ , +, *) and the asymptotically reduced model (solid lines). Here $\Lambda = L/5 = 51.2b$ and $\Delta \zeta = 0.75\zeta$.

Figure 5.5 shows the applied zeta potential in the top pane and the solute distribution \bar{c} at $t\bar{u}/2b = 15$ for $\Lambda = L/5 = 51.2b$ in the center pane. The predictions of the asymptotically reduced model and the three-dimensional model are in good agreement in the center pane. The bottom pane shows that the asymptotically reduced model can be used to obtain solute distribution at each cross-section. The cross-sectional distributions at three axial locations are calculated from direct simulation in the three-dimensional model and by use of Equation (5.21) in the asymptotically reduced model. The two types of results are in good agreement.

5.5. Summary

In Section 5.1, the problem of dispersion under axially variable conditions has been motivated from the fact that EOF in CE and CEC separations can be axially variable. In Section 5.2, we have generalized the analysis of the last chapter to calculate the dispersion of the solute with adsorption-desorption when the channel geometry and the background flow can have a slow axial variation. In Section 5.3, we have specialized the asymptotically reduced model for axially variable electroosmotic flow in a microchannel. The axial scale of this flow permits the use of lubrication approximation [**31**] for flow in the asymptotically reduced model. In Section 5.4, we have further solved the transport problem in a rectangular channel, when the axially variable EOF is caused by a periodic variation of zeta potential on its walls through direct numerical solution and compare the results with results from the asymptotically reduced model.

CHAPTER 6

Conclusions

The problems of electroosmotic flow under variable wall zeta potential and dispersion of a solute in presence of wall interactions have been addressed in this dissertation, motivated by applications in microfluidic separations like capillary electrophoresis and open channel capillary electrochromatography. Chapter 3 dealing with the fluid flow problem and Chapters 4 and 5 dealing with the dispersion problem form the core of this dissertation, while Chapters 1 and 2 form the background material.

Axially variable electroosmotic flows, wall interactions and enhanced dispersion are commonly occurring phenomena in microfluidic separations that demand our better understanding than available from the current literature. The major contributions of this research to that end are listed below:

- (i) the electroosmotic flow field in a rectangular microchannel has been simulated numerically under several representative zeta potential distributions on the wall and compared to results from the lubrication theory developed in [31].
- (ii) A theoretical model to asymptotically reduce the three-dimensional transport problem of a solute in microchannels with wall interaction to one dimension has been developed. Following are the important characteristics of this asymptotically reduced model :

- (a) The dispersion of the solute can be studied in various cross-sectional shapes (e.g. square, trapezoid, circle) and under various types of flow fields (e.g. pressure-driven, electroosmotic), by utilizing a simple shape function based approach.
- (b) The axial distribution of area averaged concentration as well as the threedimensional concentration distribution can be predicted.
- (c) For the first time in the literature, a slow axial variation in the flow field and the channel cross-sectional shape can be accommodated.
- (d) The kinetics of the wall interaction is assumed to have a general form that can accommodate slow or fast, reversible or irreversible, linear or nonlinear wall interactions.
- (e) Applications to several types of chromatographic separations can be deduced as a special case, when the adsorption and desorption is fast.
- (iii) Representative transport problems have been solved by direct numerical simulation to ascertain the accuracy of the asymptotically reduced model.

The work discussed in Chapter 3 has been published in [82]. The work described in Chapters 4 and 5 has been submitted for publication.

The following are the major conclusions and recommendations from this research:

(i) On the basis of comparisons with the numerically calculated flow field in rectangular microchannels, the lubrication theory was found to be valid beyond its formal zone of validity, being reasonably accurate in its predictions even when the zeta potential perturbation on the wall has a characteristic wavelength of the order of (but not less than) one channel width.

- (ii) When the characteristic wavelength of the zeta potential perturbation on the wall is smaller than the channel width, the lubrication theory is inaccurate, but in that case, the electroosmotic flow field in a rectangular channel can be approximated by that in a plane channel and the latter approximation gets better with progressively smaller wavelengths.
- (iii) The dispersion and solute concentration distribution predicted by the asymptotically reduced model compare favorably with those from direct numerical simulation, if the temporal variations in the problem are taking place on a time scale slow in comparison to the characteristic cross-channel diffusion time and axial variations in the problem are taking place on a spatial scale large in comparison to the channel width. These conditions are usually met in microfluidic separations, because the width to length ratio of a typical microchannel is very small.
- (iv) The asymptotically reduced model is computationally much less expensive than direct numerical solution and can serve a viable alternative to the latter in analyzing and designing microfluidic separation systems.

The work in this dissertation leaves pointers to several future research directions. The axially variable transport problem solved numerically involved a prescribed flow field and no wall adsorption. It is speculated that when proteins and peptides get adsorbed to the wall during capillary electrophoresis, an axially variable EOF dynamically coupled to the adsorption process and solute transport is generated [52]. In [52], the coupled flow transport problem is solved in an axisymmetric cylinder and a linear relationship between zeta potential and adsorbed surface concentration is assumed. It should be possible to apply our asymptotically reduced model to this kind of problems in other geometries like the rectangular channel.

There are other novel possibilities for the application of the theoretical and numerical tools developed. The flow circulations set forth by axial variation of zeta potential, as observed numerically and theoretically in Chapter 3 has mixing applications, see for example [88]. The development in Chapter 5 on transport with adsorption in axially variable channels could be applied to understand the recently developed technique of nano-scale chromatography with an Atomic Force Microscope tip, which touches the substrate at an angle [89]. This analysis may be also useful in modeling circular chromatography with electroosmotic micro-pumping [81] and shear-driven chromatography [79] in rectangular channels; some expressions for effective dispersion coefficients valid in plane channels for these techniques are already presented in Chapter 4. The developed asymptotic techniques for the transport problem in this dissertation are also applicable to various non-microfluidic systems where Taylor-Aris dispersion play a role such as transport of brine through rock fractures [64] and dispersion of silt and pollutants in rivers and estuaries [90] and dispersion of oxygen and contaminants in the pulmonary system [91].

References

- R. Probstein. *Physicochemical Hydrodynamics*. John Wiley and Sons, Inc., New York, U.S.A., 1994.
- [2] J.L. Anderson. Colloid transport by interfacial forces. Ann. Rev. Fluid Mech., 21:61–99, 1989.
- [3] J.D. Watson, T.A. Baker, S.P. Bell, A. Gann, M. Levine, and R. Losick. *Molecular Biology of the Gene*. Cold Spring Harbor Laboratory Press, Benjamin Cummings, San Francisco, U.S.A., 2004.
- [4] W.C. Brumley and Brownrigg C.M. Qualitative analysis of environmental samples for aromatic sulfonic acids by high performance capillary electrophoresis. *Journal of Chro*matography, 603:267, 1992.
- [5] A. Tiselius. A new apparatus for electrophoretic analysis of colloidal mixtures. *Transactions of Faraday Society*, 33:524, 1937.
- [6] H.A. Stone, A.D. Stroock, and A. Ajdari. Engineering flows in small devices: Microfluidics toward a lab-on-a-chip. Ann. Rev. Fluid Mech., 36:381–411, 2004.
- [7] S. Ghosal. Electrokinetic flow and dispersion in capillary electrophoresis. Annual Review of Fluid Mechanics, 38(1):309–338, 2006.
- [8] P. Tabeling. Introduction to Microfluidics. Oxford University Press, 2005.
- [9] G.I. Taylor. Dispersion of soluble matter in solvent flowing slowly through a tube. Proc. Roy. Soc. A, 219:186–203, 1953.
- [10] R. Aris. On the dispersion of a solute in a fluid flowing through a tube. Proc. Roy. Soc. A, 235:67–77, 1956.
- [11] N.W. Smith and A. S. Carter-Finch. Electrochromatography. Journal of Chromatography A, 892:219–255, 2000.

- [12] H. Ren, A.E. Karger, F. Oaks, S. Menchen, G.W. Slater, and G. Drouin. Separating dna sequencing fragments without asieving matrix. *Electrophoresis*, 20:2501–2509, 1999.
- [13] NW Smith and MB Evans. The analysis of pharmaceutical compounds using electrochromatography. Chromatographia, 38:649–657, 1994.
- [14] A.T. Conlisk. The Debye-Hueckel approximation: Its use in describing electroosmotic flow in micro- and nanochannels. *Electrophoresis*, 26(10):1896–1912, 2005.
- [15] S. Ghosal. Lubrication theory for electroosmotic flow in a channel of slowly varying cross-section and wall charge. J. Fluid Mech., 459:103–128, 2002.
- [16] A. Ajdari. Electro-osmosis on inhomogeneously charged surfaces. Phys. Rev. Lett., 75:755–758, 1995.
- [17] Shankar Devasenathipathy, Juan G. Santiago, and Kohsei Takehara. Particle tracking techniques for electrokinetic microchannel flows. *Analytical Chemistry*, 74:3704–3713, 2002.
- [18] A. Ajdari. Generation of transverse fluid currents and forces by an electric field: Electroosmosis on charge-modulated and undulated surfaces. *Phys. Rev. E*, 53:4996–5005, 1996.
- [19] M.S. Munson, M.S. Hasenbank, E. Fu, and P. Yager. Suppression of non-specific adsorption using sheath flow. *Lab Chip*, 4(5):438–45, 2004.
- [20] J.K. Towns and F.E. Regnier. Impact of polycation adsorption on efficiency and electroosmotically driven transport in capillary electrophoresis. *Anal. Chem.*, 64:2473–2478, 1992.
- [21] M. Rabe, J. Zimmermann, D. Verdes, and S. Seeger. Specific and Non-specific adsorption of Proteins on Solid Interfaces. To be presented at NSTI Nanotech 2007, Santa Clara, CA, May 2007.
- [22] S.V. Ermakov, M.Y. Zhukov, L. Capelli, and P.G. Righetti. Wall adsorption in capillary electrophoresis experimental study & computer simulation. J. Chromatography A, 699:297–313, 1995.
- [23] M.R. Schure and A.M. Lenhoff. Consequences of wall adsorption in capillary electrophoresis: Theory & simulation. Analytical Chemistry, 65:3024–3037, 1993.
- [24] M. Štědrý, B. Gaš, and E. Kendler. Dynamics of peak dispersion in capillary zone electrophoresis including wall adsorption: ii. exact analysis of unsteady linear adsorptive dispersion. *Electrophoresis*, 16:2027–2033, 1995.

- [25] J.C. Giddings. Dynamics of Chromatography, Part I, Principles and Theory. Marcel Dekker, Inc., New York, U.S.A., 1965.
- [26] L.R. Snyder and J.J. Kirkland. Introduction to modern liquid chromatography. Wiley New York, 1979.
- [27] A. Guttman and A.S. Rathore. *Electrokinetic Phenomena: principles and applications* in analytical chemistry and microchip technology. MARCEL DEKKER INC, 2004.
- [28] M.J.E. Golay. In Contribution to the Gas Chromatography Symposium, Amsterdam, 1958.
- [29] J.C. Giddings. Generation of variance, "theoretical plates," resolution, and peak capacity in electrophoresis and sedimentation. *Separation Science*, 4(3):181–189, 1969.
- [30] K. Brogle, RM Ornaf, D. Wu, and PJ Palermo. Peak fronting in reversed-phase highperformance liquid chromatography: a study of the chromatographic behavior of oxycodone hydrochloride. J Pharm Biomed Anal, 19(5):669–78, 1999.
- [31] S. Ghosal. The effect of wall interactions on capillary zone electrophoresis. J. Fluid Mech., 491:285–300, 2003.
- [32] R.P. Feynmann, R. B. Leighton, and M. Sands. The Feynmann Lectures on Physics, Volume 2. Addison Wesley, Menlo Park, U.S.A., 1970.
- [33] L.D. Landau and E.M. Lifshitz. *Course of theoretical physics Vol 10. Physical Kinetics*. Butterworth-Heinenann, Oxford, U.K., 2002.
- [34] B.J. Kirby and E.F. Hasselbrink. Zeta potential of microfluidic substrates: 2. data for polymers. *Electrophoresis*, 25:203–213, 2004.
- [35] G. Gouy. Sur la constitution de la électrique à la surface d'un electrolyte. J. Phys. Radium, 9:457–468, 1910.
- [36] D.L. Chapman. A contribution to the theory of electroencapillarity. *Phil. Mag.*, 25(6):475–481, 1913.
- [37] Victor P. Andreev, Sergeu G. Dubrovsky, and Yuri V. Stepanov. Mathematical modeling of capillary electrophoresis in rectangular channels. *Journal of Microchemical Separation*, 9:443–450, 1997.
- [38] M. Van Dyke. Perturbation Methods in Fluid Mechanics. The Parabolic Press, Stanford, USA, 1975.

- [39] F.A. Morrison Jr. Electrophoresis of a particle of arbitrary shape. J. Coll. Int. Sci., 34(210-214):45-54, 1970.
- [40] Didier Long, Howard A. Stone, and Armand Ajdari. Electroosmotic flows created by surface defects in capillary electrophoresis. *Journal of Colloid and Interfacial Science*, 212:228–349, 1999.
- [41] S. Ghosal. Band broadening in a microcapillary with a stepwise change in the ζ -potential. Anal. Chem., 74(16):4198–4203, 2002.
- [42] A.D. Stroock, M. Weck, D.T. Chiu, W.T.S. Huck, P.J.A. Kenis, R.F. Ismagilov, and G.M. Whitesides. Patterning electro-osmotic flow with patterned surface charge. *Phys. Rev. Lett.*, 8415:3314–3317, 2000.
- [43] A.D. Stroock, S.K.W. Dertinger, A. Ajdari, I. Mezic, H.A. Stone, and G.M. Whitesides. Chaotic mixer for microchannels. *Science*, 295:647–651, 2001.
- [44] R. Qiao and N. R. Aluru. Dispersion control in nano-channel systems by localized ζ potential variations. Sensors and Actuators A, 104:268–274, 2003.
- [45] J.L. Anderson and W.K. Idol. Electroosmosis through pores with nonuniformly charged walls. Chem. Eng. Commun., 38:93–106, 1985.
- [46] D. Long, H.A. Stone, and A. Ajdari. Electroosmotic flows created by surface defects in capillary electrophoresis. J. Coll. Int. Sci., 212:338–349, 1999.
- [47] R. Sadr, M. Yoda, Z. Zheng, and A. T. Conlisk. An experimental study of electroosmotic flow in rectangular microchannels. *Journal of Fluid Mechanics*, 506:357–367, 2004.
- [48] A. T. Conlisk, Jennifer McFerran, Zhi Zheng, and Derek Hansford. Mass transfer and flow in electrically charged micro- and nanochannels. *Analytical Chemistry*, 74:2139– 2150, 2002.
- [49] G. Batchelor. An Introduction to Fluid Dynamics. Cambridge Univ. Press, Cambridge, U.K., 2000.
- [50] S. Ghosal. Effect of analyte adsorption on the electroosmotic flow in microfluidic channels. Analytical Chemistry, 74(4):771–775, 2002.
- [51] J.K. Towns and F.E. Regnier. Capillary electrophoretic separations of proteins using nonionic surfactant coatings. Anal. Chem., 91:1126 – 1132, 1992.

- [52] K. Shariff and S. Ghosal. Peak tailing in electrophoresis due to alteration of the wall charge by adsorbed analytes: Numerical simulations and asymptotic theory. *Analytica Chimica Acta*, 507:87–93, 2003.
- [53] B. Gaš and E. Kendler. Dispersive phenomena in electromigration separation methods. *Electrophoresis*, 21:3888–3897, 2000.
- [54] B. Gaš, M. Štědrý, A. Rizzi, and E. Kendler. Dynamics of peak dispersion in capillary zone electrophoresis including wall adsorption: I. theoretical model and results of simulation. *Electrophoresis*, 6:958–967, 1995.
- [55] J.I. Molho, A.E. Herr, B.P. Mosier, J.G. Santiago, and T.W. Kenny. Optimization of turn geometries for microchip electrophoresis. *Anal. Chem.*, 73(6):1350–1360, 2001.
- [56] S.K. Griffiths and R.H. Nilson. Design and analysis of folded channels for chip-based separations. Anal. Chem., 74(13):2960–2967, 2002.
- [57] J.H. Knox. Thermal effects and band spreading in capillary electro-separation. Chromatographia, 26:329–337, 1988.
- [58] E. Grushka, R.M. McCormick, and J.J. Kirkland. Effect of temperature gradients on the efficiency of capillary zone electrophoresis separations. *Anal. Chem.*, 61:241–246, 1989.
- [59] V.P. Andreev and E.E. Lisin. Investigation of the electroosmotic flow effect on the efficiency of capillary electrophoresis. *Electrophoresis*, 13:832–837, 1992.
- [60] GL Erny, ET Bergstrom, and DM Goodall. Electromigration dispersion in capillary zone electrophoresis. Experimental validation of use of the Haarhoff-Van der Linde function. J Chromatogr A, 959(1-2):229–39, 2002.
- [61] B. Gaš, M. Stědrý, and E. Kendler. Peak broadening in capillary zone electrophoresis. *Electrophoresis*, 18:2123–2133, 1997.
- [62] H. Brenner and D.A. Edwards. *Macrotransport Processes*. Butterworth-Heinemann, 1993.
- [63] PC Fife and KRK Nicholes. Dispersion in Flow Through Small Tubes. Proceedings of the Royal Society of London. Series A, Mathematical and Physical Sciences, 344(1636):131– 145, 1975.
- [64] B.W. Bloechle. On the Taylor Dispersion of Reactive Solutes in a Parallel-Plate Fracture-Matrix System. PhD thesis, University of Colorado, 2001.

- [65] H. Tennekes and JL Lumley. A First Course in Turbulence, 1972.
- [66] V. Balakotaiah and H.C. Chang. Dispersion of Chemical Solutes in Chromatographs and Reactors. *Philosophical Transactions: Physical Sciences and Engineering*, 351(1695):39– 75, 1995.
- [67] GN Mercer and AJ Roberts. A Centre Manifold Description of Contaminant Dispersion in Channels with Varying Flow Properties. SIAM Journal on Applied Mathematics, 50(6):1547–1565, 1990.
- [68] R. Sankarasubramanian and W.N. Gill. Unsteady convective diffusion with interphase mass transfer. Proc. R. Soc. A, 333:115–132, 1973.
- [69] E.M. Lungu and H.K. Moffatt. The effect of wall conductance on heat diffusion in duct flow. J. Engg. Math., 16:121–136, 1982.
- [70] R. Aris. On the dispersion of a solute by diffusion, convection and exchange between phases. Proc. Roy. Soc. A, 252:538–550, 1959.
- [71] M. D. Bryden and H. Brenner. Multiple-timescale analysis of Taylor dispersion in converging and diverging flows. *Journal of Fluid Mechanics*, 311:343–359, 1996.
- [72] M. Pačes, J. Kosek, M. Marek, U. Tallarek, and A. Seidel-Morgenstern. Mathematical modelling of adsorption and transport processes in capillary electrochromatography: Open-tubular geometry. *Electrophoresis*, 24:380–389, 2003.
- [73] S.V. Patankar. Numerical Heat Transfer and Fluid Flow. Hemisphere Publishing Corporation, 1980, pp. 126.
- [74] H.K. Versteeg and W. Malalasekera. An Introduction to Computational Fluid Dynamics: The Finite Volume Method. Prentice Hall, 1995, pp. 203-205.
- [75] J.P. McEldoon and R. Datta. Analytical solution for dispersion in capillary liquid chromatography with electroosmotic flow. Anal. Chem., 64:227–230, 1992.
- [76] D. Dutta and D.T. Leighton. A low dispersion geometry for microchip separation devices. Anal. Chem., 74:1007–1016, 2002.
- [77] J.H. Ferziger and M. Peric. Computational methods for fluid dynamics. Springer New York, 2002.
- [78] A.E. Barron and H.W. Blanch. Dna separations by slab gel and capillary electrophoresis: theory and practice. Separation & purification methods, 24(1):1–118, 1995.

- [79] G. Desmet and GV Baron. On the possibility of shear-driven chromatography: a theoretical performance analysis. J Chromatogr A, 855(1):57–70, 1999.
- [80] A. Ajdari. Electrokinetic'ratchet'pumps for microfluidics. Applied Physics A: Materials Science & Processing, 75(2):271–274, 2002.
- [81] S. Debesset, CJ Hayden, C. Dalton, JCT Eijkel, and A. Manz. An AC electroosmotic micropump for circular chromatographic applications. *Lab Chip*, 4:396–400, 2004.
- [82] S. Datta, S. Ghosal, and NA Patankar. Electroosmotic flow in a rectangular channel with variable wall zeta-potential: Comparison of numerical simulation with asymptotic theory. *Electrophoresis*, 27(3):611–619, 2006.
- [83] P.C. Chatwin and P.J. Sullivan. The effects of aspect ratio on longitudinal diffusivity in rectangular channels. *Journal of Fluid Mechanics*, 120:347–358, 1982.
- [84] S.C. Jacobson, R. Hergenroeder, L.B. Koutny, and J.M. Ramsey. Open Channel Electrochromatography on a Microchip. Analytical Chemistry, 66(14):2369–2373, 1994.
- [85] Germund Dahlquist. Numerical Methods. Courier Dover Publications, 2003, pp. 349.
- [86] C. Yang and D. Li. Analysis of electrokinetic effects on the liquid flow in rectangular microchannels. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 143(2):339–353, 1998.
- [87] J.A. Wilkins and C. Horváth. Capillary electrochromatography of peptides and proteins. *Electrophoresis*, 25:2242–2256, 2004.
- [88] C.Y. Lee, G.B. Lee, L.M. Fu, K.H. Lee, and R.J. Yang. Electrokinetically driven active micro-mixers utilizing zeta potential variation induced by field effect. *Journal of Micromechanics and Microengineering*, 14(10):1390–1398, 2004.
- [89] M.S. Anderson. Microfluidics and chromatography with an atomic force microscope. Analytical chemistry(Washington, DC), 77(9):2907–2911, 2005.
- [90] PC Chatwin and CM Allen. Mathematical Models of Dispersion in Rivers and Estuaries. Annual Review of Fluid Mechanics, 17(1):119–149, 1985.
- [91] J.B. Grotberg. Respiratory fluid mechanics and transport processes. Annual Review of Biomedical Engineering, 3(1):421–457, 2001.
- [92] G.F. Roach. *Green's Functions*. Cambridge University Press, 1982.

APPENDIX A

Derivation of Equation (5.15)

By the definition of derivative:

(A.1)
$$\frac{\partial \left(\int_{\Omega} F dA\right)}{\partial X} = \lim_{\Delta X \to 0} \frac{\int_{\Omega(X + \Delta X)} F(X + \Delta X) dA - \int_{\Omega(X)} F(X) dA}{\Delta X}$$

The first integral in Equation (A.1) can be split into:

(A.2)

$$\int_{\Omega(X+\Delta X)} F(X+\Delta X) dA = \int_{\Omega(X)} F(X+\Delta X) dA + \int_{\{\Omega(X+\Delta X)-\Omega(X)\}} F(X+\Delta X) dA.$$

The domain of integration $\{\Omega(X + \Delta X) - \Omega(X)\}$ for the second integral above is a thin annulus on the $\Omega(X + \Delta X)$ plane, as shown in Figure (5.1). The differential area element of this annulus is -ldXds, if the channel cross-section varies slowly. Therefore:

(A.3)
$$\int_{\{\Omega(X+\Delta X)-\Omega(X)\}} F(X+\Delta X)dA = \Delta X \oint_{\partial\Omega} F(X)ld\underline{s} + O(\Delta X)^2.$$

Using Equation (A.3) in (A.2) and the result in (A.1) we get

(A.4)
$$\frac{\partial \left(\int_{\Omega} F dA\right)}{\partial X} = \int_{\Omega} \frac{\partial F}{\partial X} dA - \oint_{\partial \Omega} F l d\underline{s}$$

after utilizing the definition of derivative of the function F(X) in variable X.

APPENDIX B

Derivation of Equations (4.43) and (5.28)

For any two functions P(y, z) and Q(y, z) which are C_2 in $\partial\Omega$, we have from Green's second identity [92]:

(B.1)
$$\int (P\nabla_{\Omega}^{2}Q - Q\nabla_{\Omega}^{2}P)dA = \oint (P\nabla_{\Omega}Q \cdot \hat{\mathbf{n}}_{\Omega} - Q\nabla_{\Omega}P \cdot \hat{\mathbf{n}}_{\Omega})d\underline{s}$$

In the above identity, choosing P as χ and Q as Ψ and using $\bar{\chi} = 1$, $\nabla_{\Omega}^{2}\chi = \frac{u}{\bar{u}} - 1$ and $\nabla_{\Omega}\chi \cdot \hat{\mathbf{n}}_{\Omega} = 0$ from Equation (5.23) and $\nabla_{\Omega}^{2}\psi = 1$ and $\nabla_{\Omega}\phi \cdot \hat{\mathbf{n}}_{\Omega} = \frac{1}{\alpha}$ from Equation (5.22) we get:

(B.2)
$$\beta = -\frac{\overline{\psi u}}{\overline{u}} = \overline{\chi}_w$$

where Equation (5.24a) has been used. This result is true for both axially variable channels in Chapter 5 and in axially invariant channels where $\frac{u}{\overline{u}} = F(y, z)$ (Chapter 4). In the notation of Chapter 4, Equation (B.2) can be written as $\overline{\Psi F} = -\overline{\chi}_w$.

To derive Equation (5.28), we choose $P = \chi_s$ and $Q = \chi_p$ in Equation (B.1) and using Equations (5.23) specialized for shear flow F_s and pressure-driven flow F_p we get:

(B.3)
$$\overline{\chi_p F_s} = \overline{\chi_s F_p}.$$