Two-liquid stratified electroosmotic flow in microchannels

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Two-liquid Stratified Electroosmotic Flow in Microchannels

BY

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School of Mechanical and Aerospace Engineering

A DISSERTATION SUBMITTED TO THE
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Abstract

Two-liquid stratified electroosmotic flow in rectangular microchannels is analyzed analytically and numerically. The two-liquid system consists of two immiscible liquids: an aqueous solution and a non-aqueous liquid. When an electric field is applied across the channel, the aqueous solution will be driven by electroosmosis, which drags the non-aqueous liquid by the hydrodynamic shear forces. The model accounts for surface charges at the liquid-liquid interface. To find the coupling effects between two liquids, which is one of important conditions, the general interfacial conservation equation is investigated. The presence of surface charge at the interface induces a jump of pressure in normal direction and a jump of stress in the tangential directions of the interface.

In the fully-developed region, the analytical solutions of two liquids combined both the electric effect and pressure gradient are obtained using the separation of variables method. The dynamic aspects of the two-liquid electroosmotic flow are studied by solving the transient governing equations using the Laplace transform method. The effects of dynamic viscosity ratio, interfacial potential, aspect ratio and parameters of the electric double layer on the flow characteristics are analyzed.

A method to control the interface between two liquids using electroosmosis is studied by theoretical and experimental investigations. Experiments were conducted to verify the proposed model. The theoretical solutions agree with the measured velocity profiles under different applied electric fields. It is shown that the electroosmotic effect can be used to control the interface position between the two fluids.

The presences of surface tension and surface charges result in jumps of pressure and stress across the interface between two liquids. Finite difference method is used to numerically capture these jump conditions within one grid. To determine the interface shape, level set method is adopted with the SIMPLER algorithm. The study provides insights into the two-liquid electroosmotic flow in microchannels.

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Contents

Abstract	ii
Acknowledgements	iii
List of Tables	viii
List of Figures	ix
List of Symbols	xviii
1 Introduction	1
1.1 Background and Motivation	1
1.2 Objective and Scope	3
1.3 Outline of the Thesis	4
2 Literature Review	5
2.1 Electrokinetic Effects in Microchannel Flow	5
2.1.1 Analytical solutions of single-fluid electroosmotic flow	5
2.1.2 Numerical simulations of single-fluid electroosmotic flow	7
2.1.3 Experimental studies of single-fluid electroosmotic flow	8
2.1.4 Design and fabrication of single-fluid electroosmotic micropumps	10
2.2 Two-phase Flow in Microchannels	11
2.3 Liquid-liquid Two-layer Electroosmotic Flow	13
2.4 Numerical Methods for Simulation of Two-phase Flow	14
3 Conservation Equations	17

3.1	Intrinsic Definition of Interface	17
3.2	Bulk Conservation Equations	18
3.2.1	Continuity equation	19
3.2.2	Momentum equation of the two liquids	19
3.3	Electric Double Layer	21
3.4	Electric Potential and Species	23
3.5	Interfacial Conservation Equations	24
3.6	Dimensionless Equations	27
4	Analytical Analysis	29
4.1	Electrical Double Layer Potential	30
4.1.1	Linearization and solution	30
4.1.2	Electrical potential distribution in the aqueous solution	33
4.2	Momentum Equations of Two-liquid Flow	36
4.3	Steady State Two-liquid Electroosmotic Flow	39
4.3.1	Analytical solutions	39
4.3.2	Results of the steady state two-liquid EOF	43
4.4	Transient Two-liquid Electroosmotic Flow	49
4.4.1	Analytical solutions	49
4.4.2	Results of the transient two-liquid EOF	55
4.5	Electroosmotic Control of the Interface between Two-liquid Flow	64
4.5.1	Interface Position	65
4.5.2	Experimental Validation	71
4.5.3	Velocity Profiles	74
5	Numerical Analysis	80
5.1	Implementation of Surface Tension and Surface Charges	81
5.2	Level Set Method	83
5.2.1	Level set function	83

5.2.2	Redistribution	85
5.3	Numerical Scheme for Jump Conditions	86
5.3.1	One dimensional case	86
5.3.2	Two dimensional case	88
5.4	SIMPLER Algorithm with Jump Interface Condition	91
5.4.1	Velocity equation	91
5.4.2	Pressure and velocity corrections	92
5.4.3	Pressure-correction equation	94
5.4.4	Pressure equation	95
5.4.5	SIMPLER algorithm	95
5.5	Numerical Analysis of Two-liquid Stratified flow	96
5.5.1	Two immiscible liquids with the same properties	96
5.5.2	Two immiscible liquids with different properties	98
5.6	Numerical Analysis of Two-liquid Stratified Electroosmotic Flow	102
5.6.1	Governing Equations	102
5.6.2	Validation of the Numerical Scheme	103
5.6.3	Two-liquid EOF Corresponding to Various Applied Electric Fields	108
6	Conclusions and Future Studies	114
6.1	Summary of Investigations	114
6.2	Future Work	117
	Publications arising from this thesis	119
A	Transport Balance Laws for Interface	121
A.1	Intrinsic definition of interface	121
A.2	Interfacial Conservation Equation	122
A.2.1	General conservation equation at a discontinuous interface	123
A.2.2	Interfacial mass balance	126

A.2.3	Stress balance with surface tension at an interface	127
B	Numerical Inversion of the Laplace Transforms	129
C	Pressure and Stress Jump across the Interface	132
D	Verification of Numerical Scheme by Heat Conduction Problem	134
D.0.4	One dimension heat conduction in two homogeneous materials with heat generation	134
D.0.5	Two dimensional heat conduction in two homogenous materials with a rectangular inside	136
D.0.6	Two dimensional heat conduction in two homogenous materials with a circle inside	138

List of Tables

B.1	Set of ten constants for V for the Gaver-Stehfest method	131
B.2	Set of twenty constants for V for the Gaver-Stehfest method	131

List of Figures

1.1	Schematic of the two-liquid electroosmotic flow.	3
3.1	Two-liquid system and the control volume including an interface, Γ . . .	18
3.2	Schematic structure of electric double layer and representation of a possible potential distribution, after Probstein [1994, p.190].	21
4.1	Schematic of the phenomenon and coordinate system	29
4.2	Electrical potential distributions.	34
4.3	Dimensionless velocity distributions at the symmetric line for different viscosity ratios.	44
4.4	Comparison of the analytical solution between the two-fluid model and the single-fluid model. The viscosity ratio between the two liquids is $\beta = 10^4$	45
4.5	Dimensionless velocity distributions at the symmetric line for different interfacial zeta potential.	46
4.6	Dimensionless velocity distributions at the symmetric line for different values of K when $\beta = 1$ and $\zeta_3 = 0.5\zeta_1$	47
4.7	Dimensionless velocity distributions at the symmetric line for different aspect ratio of pure electroosmotic flow.	48

4.8	Dimensionless velocity distributions at the symmetric line for different aspect ratio of pure pressure driven flow. For $chi = 1$, the dimensionless pressure gradient is $d\bar{p}/d\bar{x} = 300$, for $\chi = 5$, $d\bar{p}/d\bar{x} = 3000$ and for $\chi = 10$, $d\bar{p}/d\bar{x} = 10^4$	49
4.9	Developing process for two-liquid electroosmotic flow ($K = 130$, $\alpha = 1.5$, $\beta = 1$ and $\zeta_1 = \zeta_2 = 0.5\zeta_3$), (continued).	57
4.9	Developing process for two-liquid electroosmotic flow ($K = 130$, $\alpha = 1.5$, $\beta = 1$ and $\zeta_1 = \zeta_2 = 0.5\zeta_3$).	58
4.10	Dimensionless transient two-liquid velocities at the symmetric line for different zeta potentials ($K = 130$, $\alpha = 1.5$ and $\beta = 1$), (continued). . . .	59
4.10	Dimensionless transient two-liquid velocities at the symmetric line for different zeta potentials ($K = 130$, $\alpha = 1.5$ and $\beta = 1$).	60
4.11	Dimensionless transient two-liquid velocities at the symmetric line for different zeta potentials ($K = 130$, $\alpha = 1.5$ and $\beta = 10$), (continued). . .	61
4.11	Dimensionless transient two-liquid velocities at the symmetric line for different zeta potentials ($K = 130$, $\alpha = 1.5$ and $\beta = 10$).	62
4.12	Dimensionless transient two-liquid velocities at the symmetric line for different value of K ($\alpha = 1.5$, $\beta = 10$ and $\zeta_3 = 0.5\zeta_1$).	63
4.13	Schematic representation of the H-shaped microchannel	65
4.14	Schematic of interface control using electroosmotic effect.	66
4.15	Schematic representation of the meaning of S_R	68
4.16	Dependence of the holdups of the aqueous solution on the externally applied electric field for different flow rates, $\beta = 1.5$, $\chi = 10$	69
4.17	Dependence of the pressure gradient on the externally applied electric field for different flow rates, $\beta = 1.5$, $\chi = 10$	69
4.18	Dependence of the holdups of the aqueous solution on the externally applied electric field for viscosity ratios, $\bar{q}_1 = \bar{q}_2 = 0.01$, $\chi = 10$	70

4.19	Dependence of the pressure gradient on the externally applied electric field for different aspect ratios, $\beta = 1.5$, $\bar{q}_1 = \bar{q}_2 = 0.01$	70
4.20	H-shaped microchannel used in the experiments.	71
4.21	Schematic of the experimental setup for fluorescence imaging and micro-PIV measurements.	72
4.22	Comparison of the holdups between calculated and experimental results.	75
4.23	Comparison between theoretical and experimental velocity profiles, (continued).	77
4.23	Comparison between theoretical and experimental velocity profiles.	78
5.1	The schematic of level set function	84
5.2	The schematic of numerical method in 1D	87
5.3	The schematic of numerical method in 2D	89
5.4	Evolution of velocity and interface profiles along x/H when $Ca = 10$ and $Re = 0.1$	97
5.5	Evolution of interface profiles along x/H for different Ca	98
5.6	Pressure distributions for two immiscible liquids with same properties.	99
5.7	Evolution of velocity and interface profiles along x/H when $Ca = 10$ and $Re = 0.1$	100
5.8	Evolution of interface profiles along x/H for different Ca	100
5.9	Pressure distributions for two immiscible liquids with different properties.	101
5.10	Schematic of successive meshes.	105
5.11	Schematic of mesh used in simulation.	105
5.12	Evolution of velocity and interface profiles along x/H and $\beta = 1$	106
5.13	Velocity profiles for various meshes when $K = 20$	107
5.14	Velocity profiles for various meshes when $K = 100$	107
5.15	The interface profiles along x/H for $\beta = 1$ and $\zeta_s = 0.1\zeta_w$	109
5.16	The velocity profiles at outlet for $\beta = 1$ and $\zeta_s = 0.1\zeta_w$	110

5.17	The interface profiles along x/H for $\beta = 5$ and $\zeta_s = 0.1\zeta_w$	111
5.18	The velocity profiles along outlet for $\beta = 5$ and $\zeta_s = 0.1\zeta_w$	112
5.19	Evolutions of velocity and interface profiles along x/H when $\beta = 5$ and $\zeta_s = 0.1\zeta_w$	113
A.1	Curvilinear orthogonal coordinates and the control volume containing the interfacial layer	123
D.1	One dimensional heat conduction problem.	135
D.2	Two dimensional heat conduction problem with a rectangular inside. . .	137
D.3	Two dimensional heat conduction problem with a circle inside.	139

List of Symbols

A_p	parameter in the analytical solution of velocity
$b1_j, b2_j$	parameters in the analytical solution of velocity
B_j	parameter in the analytical solution of velocity
Ca	Capillary number, defined as $Ca = \frac{\mu V_{\text{ref}}}{\sigma}$
e	elementary charge, $e = 1.602 \times 10^{-19}$, [C]
$\mathbf{E}$	electric field strength, $\mathbf{E} = -\nabla\Phi$, [NC ⁻¹]
E_x	electric field strength in x-direction, [NC ⁻¹]
$\mathbf{f}$	body force, [Nm ⁻³]
F	the function of an intrinsic definition of a interface
$\mathbf{G}$	parameter measuring the electroosmotic force by external electric field, $\mathbf{G} = \frac{2n_0 z_0 e L_{\text{ref}} \mathbf{E}}{\rho_{\text{ref}} V_{\text{ref}}^2}$
G_x	x-direction of $\mathbf{G}$
G_s^n	parameter measuring the strength of applied electric field on the pressure jump
G_s^t	parameter measuring the strength of applied electric field on the stress jump
h, H	height of the microchannel, [m]
h_1, h_2	height of the aqueous solution and non-aqueous liquid, respectively, [m]
$\mathbf{I}$	identity tensor

$\mathbf{I} - \mathbf{nn}$	tangential projection tensor
$\mathbf{J}$	transport flux
$\mathbf{J}_{ }^s$	interfacial transport flux
k_b	Boltzmann constant, $k_b = 1.381 \times 10^{-23}$ [JK ⁻¹]
K	electrokinetic parameter, $K = \kappa L_{\text{ref}}$
L	length of the microchannel, [m]
$\dot{m}$	mass flux across the interface [kgs ⁻¹ m ⁻²]
$\dot{m}_{\text{cor}}$	mass correction factor
M	electrokinetic effect in the matching conditions, $M = \frac{\epsilon k_b T E_x}{z_0 e U_{\text{ref}} \mu_{\text{ref}}}$
n_0	ionic number concentration in the bulk, [m ⁻³]
n_k	ionic number concentration of the type- i ion, [m ⁻³]
n_1, n_2	normal vector in x and y-direction respectively
$\mathbf{n}$	outward unit normal
$\mathbf{nn}$	normal projection tensor
p	pressure, [Pa]
$\mathbf{r}$	position vector, [m]
R_j	thermal contact resistance, [KW ⁻¹]
Re	Reynolds number, $\frac{\rho_{\text{ref}} V_{\text{ref}} L_{\text{ref}}}{\mu_{\text{ref}}}$
s	Laplace transform parameter
S_R	parameter to measure electroosmotic force related to pressure gradient, defined as $S_R = \text{Re} G_x \bar{\zeta}_2 / K$
t	time, [s]
t_1, t_2	tangential vector in x and y-direction respectively
$\mathbf{t}$	unit tangential
T	absolute temperature, [K]
$\mathbf{T}$	stress tensor, [Nm ⁻²]

$\mathbf{T}^M$	Maxwell's stress tensor, $[\text{Nm}^{-2}]$
$\mathbf{T}'$	viscosity stress tensor, $\mathbf{T}' = \mu(\nabla \mathbf{v} + \nabla \mathbf{v}^T)$, $[\text{Nm}^{-2}]$
u	velocity in x-direction, $[\text{ms}^{-1}]$
U	Laplace transform of u
v	velocity in y-direction, $[\text{ms}^{-1}]$
$\mathbf{v}$	velocity vector, $[\text{ms}^{-1}]$
$\mathcal{V}$	a control volume
$\partial \mathcal{V}$	boundary of the control volume $\mathcal{V}$
w	width of the microchannel, $[\text{m}]$
$\mathbf{w}^s$	velocity of the control volume across the interface $[\text{m/s}]$
$w_{\perp}^s$	normal velocity of the surface $[\text{m/s}]$
x, y, z	coordinate directions $[\text{m}]$
z_k	valence of the type- i ion

Greek symbols

α	kinetic viscosity ratio, defined as ν_2/μ_1
β	viscosity ratio, defined as μ_2/μ_1 ; it is also the coefficient in Poisson's equations
$\hat{\beta}$	revised coefficient at the interface
δ	thickness of the aqueous solution in microchannels
δ_{in}	height of the aqueous solution at the inlet
δ_{ij}	Kronecker delta
ϵ	permittivity of the solution, $\epsilon = \epsilon_r \epsilon_0$, $[C^2 N^{-1} m^{-2}]$
ϵ_0	permittivity of vacuum, $\epsilon_0 = 8.85 \times 10^{-12} [C^2 N^{-1} m^{-2}]$
ϵ_r	dielectric constant of the solution
$\varepsilon_1, \varepsilon_2$	hold up of the aqueous solution and the non-aqueous liquid, respectively

ζ_{ref}	reference zeta potential, $[NmC^{-1}]$
$\zeta_1, \zeta_2, \zeta_3$	zeta potential at the bottom wall, side wall and interface respectively, $[NmC^{-1}]$
ζ_w, ζ_s	zeta potential at the wall and the interface, $[NmC^{-1}]$
θ	any property in bulk
θ^s	any interfacial property
$\dot{\theta}$	volumetric production of the property in bulk
$\dot{\theta}^s$	volumetric production of the interfacial property
κ	Debye-Hückel parameter $[m^{-1}]$
λ_j	parameter in the analytical solution of velocities
μ	fluid's viscosity, $[Nsm^{-2}]$
ν	kinematic viscosity, $[ms^{-1}]$
ξ	redistribution function
ξ'	second redistribution function
Ω	domain of the general equation
ρ	mass density, $[kgm^{-3}]$
ρ^s	interfacial mass density, $[kgm^{-2}]$
ρ_q	net volume charge density, $[Cm^{-3}]$
ρ_q^s	interfacial charge density, $[Cm^{-2}]$
ρ_{qw1}^s	surface charge density at the bottom wall, $[Cm^{-2}]$
ρ_{qw2}^s	surface charge density at the side wall, $[Cm^{-2}]$
σ	surface tension, $[Nm^{-1}]$
τ	pseudo time
ϕ	level set function
$\Phi_j(\bar{y}), \Phi_j(\bar{y}, s)$	parameter function
$\Phi_j'(\bar{y}), \Phi_j'(\bar{y}, s)$	parameter function
χ	aspect ratio
ψ	electrical potential in the diffuse layer, $[NmC^{-1}]$

Subscripts

1, 2	aqueous solution and non-aqueous liquid, respectively
I, II	fluid 1 and fluid 2, respectively
e	quantity at the surface e
E	quantity at the grid point E
n	quantity at the surface n
N	quantity at the grid point N
P	quantity at the grid point P
s	quantity at the surface s
S	quantity at the grid point S
w	quantity at the surface w
W	quantity at the grid point W
ref	reference quantity

Superscripts

*	guessed quantity in numerical algorithm
—	dimensionless parameter
E	corresponding to the electroosmotic force
P	corresponding to the pressure gradient

Operators

$\frac{d_{\mathbf{w}^s}}{dt}$	material derivative, $\frac{d_{\mathbf{w}^s}}{dt} = \frac{\partial}{\partial t} + \mathbf{w}^s \cdot \nabla$
$[[\theta]]$	jump quantity between the two values of θ across the interface, $[[\theta]] = \theta_2 - \theta_1$
$[[\theta]]_+$	average quantity between the two values of θ across the inter- face, $[[\theta]] = \frac{1}{2}(\theta_2 + \theta_1)$

∇	gradient
∇_s	surface gradient

Chapter 1

Introduction

1.1 Background and Motivation

Microfluidics involves flow of liquids and gases, single or multiphase, through microdevices fabricated by Micro Electro-Mechanical Systems (MEMS) technology. Micropumps, micromixer, microturbines and microvalves [Gad-el-Hak, 1999; Shoji and Esashi, 1994] are examples of microfluidic devices. Microfluidics has grown recently, fostered by the development of lab-on-a-chip devices, i.e. systems able to perform an impressive number of tasks on a small chip, such as mixing and separating samples, chemical reactions and analyzing and detecting molecules. In the next few years, a variety of such systems, designed to identify a particular odor or analyze the DNA from a drop of blood, or a piece of cheese, will likely be made available [Tabeling, 2001]. In addition, microfluidics is also involved in many other applications, such as propulsion of miniaturized rockets, cooling of Large Scale Integrated Circuit (LSIC), Proton-Exchange Membrane (PEM) fuel cells, inkjet print heads and so on.

Microfluidic devices possess unique advantages. Owing to its small dimensions, such devices are ideal for handling costly and difficult-to-obtain samples and reagents in medical and bio-analyze. A typical microfluidic structure requires samples and reagents of 100nl and 10nl. MEMS sensors for pressure, velocity, temperature and shear stress are

at least one order of magnitude smaller than conventional sensors. Their small size improves both the spatial and temporal resolutions of the measurement, typically few microns and few microseconds, respectively. Moreover, the microsensors' extreme miniaturization and low energy consumption make them ideal for monitoring the flow state without appreciably affecting it.

Micropump is a kernel component in microfluidic devices to provide the kinetic source to route the liquid through microchannels. As one of non-mechanical pumps, the electroosmotic (EO) micropump has many advantages over other types of micropumps. First, EO micropumps have no moving solid parts and have much simpler designs as compare to the typical mechanical micropumps. Second, precise amounts of liquid can be maneuvered by easily controlling the externally applied electric field.

The physical mechanism underling the EO micropump is electroosmotic flow (EOF). Electroosmotic flow refers to a liquid flow induced by an external electric field. The discovery of electroosmotic flow may be credited to F. F. Reuss, whose experiments on electroosmosis and electrophoresis were described in 1809 [Probstein, 1994, p. 195]. Electroosmosis has been used in a variety of applications, including the dewatering of soils for construction purposes and the dewatering of mine tailings and waste sludges. Electroosmosis is also being investigated as a mean of removing contaminants from soils Hunter [1988]. Recently, with the development of microfluidic devices, electroosmosis has drawn a wide attention due to its fluid controlling ability.

To induce electroosmosis, however, the working liquid is required to be an aqueous solution with significant electrical conductivity. Non-aqueous liquids such as oil cannot be pumped using the electroosmosis due to the low electrical conductivity [Brask et al., 2003; Goranović, 2003]. On the other hand, in some biochemical analysis, the EO pumps may not be suitable to be used directly with the water solutions. This is because that the voltage applied to the solutions can lead to undesirable problems, i.e., the electrochemical decomposition of the solute, the fluctuation of the pH of the buffer solution and the generation of gases [Watanabe et al., 2003].

Figure 1.1: Schematic of the two-liquid electroosmotic flow.

After a broad review of the currently available literature on EOF, it can be concluded that most of the studies done so far focus on the single-liquid EOF. The system we present here are termed *two-liquid stratified electroosmotic flow* as shown in Fig. 1.1. This system consists of two immiscible liquids: an aqueous solution at the lower section and a non-aqueous liquid at the upper section of the channel in Fig. 1.1. When an electric field is applied across the aqueous liquid, the liquid will be driven by electroosmosis, which drags the non-aqueous liquid by the hydrodynamic shear force.

1.2 Objective and Scope

This study is to investigate the characteristics of the two-liquid stratified electroosmotic flow in microchannels. The objectives of the proposed project are:

- to study and characterize the two-fluid stratified flow driven by electroosmotic force, especially, the interfacial balance conditions.
- to formulate and derive analytical solutions for the case of a fully-developed two-liquid stratified electroosmotic flow, which provides a benchmark for further study.
- to develop a numerical scheme for two-fluid electroosmotic flow, which considers both the surface tension and surface charge as *excess* quantities at the interface.

1.3 Outline of the Thesis

There are six chapters in this thesis. Chapter 1 gives an introduction to the two-liquid stratified electroosmotic system and a description of the objectives and the scope of this project. In Chapter 2, literature review is provided to focus on the electroosmotic flow in microchannels and the numerical methods to simulate two-fluid flow.

Chapters 3 serves as the mathematical fundamental of this study. The bulk governing equations and the interfacial balance equations including the electric effects are presented in this chapter.

In Chapter 4, the solutions of Poisson-Boltzmann equation and two-liquid electroosmotic flow are solved analytically in the fully developed region. The results provide more insight into the characteristics of such flow. A method to control the interface between two liquids by electroosmosis is presented in this chapter. Predictions from the mathematical model are validated by experimental results.

In Chapter 5, level set method (LSM) is presented for numerical simulation of the two-fluid flow. The evolution of interface is captured by the level set function. The major work is to integrate the electrokinetic effects and the level set function into SIMPLER scheme. Meanwhile, to deal with the surface tension and surface charge such *excess* quantities at the interface, the interface balance laws are incorporated in the numerical model. The presence of the excess quantities induces jump conditions across the interface. Chapter 5 also presents the numerical results of two-liquid electroosmotic flows. The liquid-liquid interface developments due to the favorably and adversely applied electric field are examined.

Finally, Chapter 6 draws the main conclusions from this study and makes recommendations for future work.

Chapter 2

Literature Review

2.1 Electrokinetic Effects in Microchannel Flow

It is well-known that most solid-liquid interfaces bear electrostatic charges - non-zero surface potential. For aqueous solutions which contain mobile ions, the electrostatic charge on the non-conducting solid surface will attract the counterions in liquid. The rearrangement of the charges on the solid and the balancing charges in the liquid is called the electrical double layer (EDL). The thickness of the EDL depends on the bulk ionic concentration and electrical properties of the liquid, varying from 1nm to 100nm. Although the thickness of EDL is very small, it plays an important role in the microscale fluidic devices.

2.1.1 Analytical solutions of single-fluid electroosmotic flow

The theory of the electrokinetic effects on microchannel flow characteristics has been well established. Burgreen and Nakache [1964] studied the effect of the surface potential on liquid transport through ultrafine capillary slits with the Debye-Hückel linear approximation to the electrical potential distribution under an imposed electrical field. Rice and Whitehead [1965] conducted research on the same problem in narrow cylindrical capillaries. Levine et al. [1975] extended the model to a higher surface potential by

developing an approximate solution of the Poisson-Boltzmann (P-B) equation.

Recently, Bowen and Jenner [1995] extended analysis of electro-viscous effects to asymmetric electrolytes in which the mobilities of anions and cations may be individually specified. They solved the nonlinear Poisson-Boltzmann equation numerically in cylindrical coordinates. It was shown that the calculated electroviscous effects are strongly dependent on the mobility of the ions of opposite charge to the capillary wall (counterions) even if the coions are kept the same.

Yang and Li [1998] presented a linear solution of a two-dimensional Poisson-Boltzmann equation in the cross-section of rectangular channels based on the Debye-Hückel approximation. An additional body force originating from the presence of the EDL was considered to modify the conventional Navier-Stokes equation. By using the Green's function formulation, an exact solution to this modified Navier-Stokes equation in the rectangular channel was obtained. They discussed the effects of EDL, channel size and the electrical static charge on the fluid velocity distribution, streaming potential, volume flow rate, friction coefficient and the apparent viscosity. The results showed that the apparent viscosity and friction coefficient are larger with EDL effects.

In another paper, Yang et al. [1998] solved the steady-state, fully-developed laminar flows, which induced streaming potential effects; both the velocity and the temperature fields in a rectangular microchannel were obtained. Their calculations indicated that the zeta potential of the solid surface and the concentrations of the electrolyte solution have a significant influence on the friction coefficient (electroviscous effects). In addition, the temperature was increased with the effects of EDL.

Dutta and Beskok [2001] presented analytical results for the velocity distribution, mass flow rate, pressure gradient, wall shear stress, and vorticity in mixed electroosmotic and pressure driven flows for a parallel plate channel. They divided the flow field into two parts: bulk and finite EDL marked by effective EDL thickness (δ_{99}), which is defined as the distance from the wall where the electroosmotic potential decays to 1% of its original value. The thin EDL was a great challenge in numerical simulation of elec-

troosmotic flow. Therefore, they presented a unified slip condition, which incorporated the EDL effects by specifying an appropriate velocity slip (Helmhotz-Smoluchowski velocity) condition on the wall. For a general numerical algorithm, implementations of this slip velocity on the boundary according to flow rate; while the velocity distribution within the EDL is neglected. (The idea is the same as the wall function in the turbulent flows situations.)

Maynes and Webb [2002] analyzed an electroosmotic flow in a parallel plate microchannel and circular microtube under the imposed constant wall heat flux and constant wall temperature boundary conditions. For the constant heat flux boundary condition, the fully developed Nusselt number was found to depend on the duct radius, Debye length, duct radius ratio and dimensionless volumetric source (due to the Joule heating). For the constant wall temperature boundary condition, the channel stream-wise asymptotic condition is one for which all energy generated volumetrically in the fluid due to Joule heating is dissipated convectively through the channels wall.

Yang and Kwok [2003] presented an analytical solution for oscillating flow in parallel-plate microchannels by combining the electrokinetic transport with Navier's slip condition. The slip length is constant as $1\mu m$ for a channel with a half height of $20\mu m$. They suggested that electrokinetic transport phenomena and liquid slip at the channel wall are both important and should be considered simultaneously. For pressure-driven flow, liquid slip counteracts the effects by the electrical double layer and induces a larger slip flow rate. If slip is neglected, a higher apparent viscosity would be predicted. For electroosmotic flow, liquid slip alters the flow rate by about 20%.

2.1.2 Numerical simulations of single-fluid electroosmotic flow

some researches focused on flows in microchannel with electrokinetic effects by numerical simulations. Patankar and Hu [1998] developed a three-dimensional numerical scheme to simulate electroosmotic flow in complicated geometries. They simulated the elec-

electroosmotic flow at the intersection of a cross-channel during the injection process. They found that the distortion of the injected sample at the intersection of the cross-channel is reduced when the injection is performed at high Reynolds numbers. The application of an electric potential at the side reservoirs can be used to control the shape of the injected sample plug.

Dutta et al. [2002a] developed a spectral element algorithm to analyze mixed electroosmotic/pressure driven flows in complex two-dimensional geometries. Using this spectral algorithm, they simulated the liquid flows in straight channels made out of two different materials. At the entry and exit portions of the channel, the material exhibits negligible electrokinetic effects. In the middle section, the materials exhibited strong electrokinetic effects. The proposed configuration has practical relevance, and it can be used as a test bed to study electroosmotic/pressure driven flows. They also explored the electroosmotic flow in a T-junction geometry under various external electric field strengths. Flow rate in the T-junction was shown to vary linearly with the electroosmotic body force in the Stokes flow regime. The Stokes flow in Y-split junctions was simulated in another paper by Dutta et al. [2002b].

2.1.3 Experimental studies of single-fluid electroosmotic flow

Some experiments were carried out to study electroosmotic flow. Werner et al. [1998] developed an experimental setup for determination of the electrokinetic potential and the surface conductivity of flat surface. The zeta potential is calculated at different channel geometries based on streaming potential and channel conductivity data. For the plasma-deposited fluoropolymer (PDFP) interfaces, zeta potential up to -100mV were obtained in solutions of neutral pH exclusively due to preferential ion adsorption.

Arulanandam and Li [2000] reported a simple procedure for determining specific surface conductance and zeta potential, based on monitoring of the electrical current in electro-osmosis. In their experiments, the average velocity was calculated by using the

measured time required to completely displace the liquid in a silicon glass capillary tube of a $100\mu m$ diameter. Their results showed the zeta potential is independent of both the channel size and the applied voltage. This was expected since zeta potential is a property of the solid surface and the electrolyte solution. The zeta potential changes with the electrolyte concentration, and the values are $-130mV$, $-100mV$ and $-80mV$ for the concentration 10^{-4} , $10^{-3}M$ and $10^{-2}M$, respectively.

In the classical method of determining the zeta potential and the surface conductance, the electrokinetic effects on the liquid flow were not considered. Erickson et al. [2000] improved the slope-intercept technique which accounts for cases where the electrokinetic effect on the flow is significant. The streaming potential data were obtained for silt glass channels, ranging in height from $3\mu m$ to $66\mu m$, in variety of solutions ranging in ionic concentration from 10^{-6} to 10^{-3} . It was confirmed that the classical technique indeed overestimates both the zeta-potential and surface conductance of the solid surface. For solutions with low ionic concentration, which has a thicker EDL, this overestimation was shown to be quite significant. As the solution ionic concentration increased and the thickness of the EDL diminished, the two methods were shown to produce nearly identical results.

Ren et al. [2001] conducted experiments to investigate the electro-viscous effects on liquid flow. Pure water, KCl solutions with bulk concentration of $10^{-4}M$ and $10^{-2}M$, $10^{-4}M$ $AlCl_3$ solution, and $10^{-4}M$ LiCl solution were conducted in silicon channels with a height of 14.1, 28.2 and $40.5\mu m$, respectively. These results showed a strong dependence of $dP/dx \sim Re$ relationship on the channel size, the ionic concentration, the ionic valence, and the bulk conductivity of the liquids. The apparent viscosity corresponding to these measured $dP/dx \sim Re$ relationship was found to be about 10% higher than the true viscosity, depending on the liquids and the ratio of the channel height to the EDL thickness.

Using a microelectrophoresis technique, Yang et al. [2001] developed an experimental rig for measuring the zeta potential of fine bubbles in aqueous solutions. The measure-

ments indicated that the variation of the bubble zeta potential with solution pH depends not only on the electrolyte concentration but also on the type of metal ions. In the case of uni-valent NaCl solutions, it was found that bubbles are by-and-large negatively charged. The presence of multi-valent metal ions such as Ca^{2+} and Al^{3+} can greatly change the magnitude of the bubble zeta potential and even reverse the bubble's charge polarity.

2.1.4 Design and fabrication of single-fluid electroosmotic micropumps

One of the main applications of electrokinetic flow is the development of electroosmotic micropump for bio-chemical analysis and microelectronic cooling systems. The pump is the core part of the fluidic devices.

Morf et al. [2001] designed an electroosmotic pump, which basically consists of a parallel arrangement of six microchannels with rectangular cross-section (83mm long, 300 μm wide and 50 μm high). A mathematical model was developed. The model fitted well with experimental data and revealed a linear relationship between the flow rate and the applied voltage.

Guenat et al. [2001] presented a micro total analysis system (μ TAS) which consisted two electroosmotic pumps. The unique feature of the integrated electroosmotic pumps is the ability to pump widely different solutions. Typical flow rates achieved in the μ TAS were in the range of 2 to 65nl/s, depending on the number of microchannels connected in parallel and on the applied voltage. In the lower voltage range, remarkably stable flows were generated, which allowed several analyses to be performed consecutively.

Zeng et al. [2001] fabricated EOF pumps by packing the 3.5 μm diameter non-porous silica particles into 500 – 700 μm diameter fused-silica capillaries and using a silicate frit fabrication scheme to hold the particles in place. The effective pore radius of 0.53 μm was derived from the experimental pressure-flowrate relationship. The zeta potential for their packed capillaries was $-95mV$. These pumps had no moving parts and could

generate maximum pressures in excess of 20 atm or maximum flow rates of $3.6\mu\text{L}/\text{min}$ for a 2kV applied potential.

Chen and Santiago [2002] fabricated an EOF pump on soda-lime glass substrate using the standard microlithography and chemical wet etching techniques. This EOF micropump can pump DI water against a high back pressure up to 1.5 atm at 3kV applied potential. The pump provides maximum pressure and flow rate performance of 0.33 atm and $1.5\mu\text{L}/\text{min}$ at 1kV with a thermodynamic efficiency of 0.49%. The experimental data showed a linear relationship between pressure and flow rate. At high electric field strengths, the flowrate was enhanced by electrical Joule heating, which also sets an upper limit of 4kV for the operating voltage of this pump.

2.2 Two-phase Flow in Microchannels

While in macrosystems body forces such as gravity is the dominant, surface force (surface tension) is negligible. In microsystems, on the other hand, gravity is negligible but surface tension becomes a dominant force. Consequently, two-phase flow in microchannels is different from that in large-scale channels.

Jiang et al. [1999] developed a technique to fabricate microchannel heat sinks integrated with a heater and an array of temperature sensors. The measurements, with DI water as the working fluid, were used to evaluate the heat sink performance under forced convection conditions. Surprisingly, the typical boiling plateau was not observed in those channels under all tested conditions. Moreover, under critical heat flux (CHF) conditions, the device temperature dependence on flow-rate and the temperature distribution was clearly a function of the channel size.

Lee et al. [2002] conducted two-phase boiling experiments with trapezoidal channels. In the experiments, temperature plateaus were observed in the boiling curves, corresponding to the latent heat of phase change of the working fluid from liquid to vapor phase. They also recorded the two-phase flow patterns using a high-speed camera. In

the triangular cross section microchannels, Jiang et al. [1999] found a stable vapor core was established at a relatively low input power, suppressing the development of bubbly flow. In trapezoidal channels, however, bubble formation, growth and detachment were rather unique when operating temperature was lower than the water saturation temperature. In classical bubble dynamics, the bubble explodes when the pressure difference overcomes the surface tension. However, due to geometric constraint in a microscale, the bubble occupies the entire channel and very long tail connects the bubble to its nucleation site. Only when the surface tension along the tail overcomes the internal pressure, does the bubble depart. This is attributed to the geometry effect on the flow pattern.

Beside the steam-water flow, some researchers studied the air-water flow in microchannels. Serizawa et al. [2002] visualized air-water two-phase flow patterns in circular tubes of 20, 25 and 100 μm diameters. The air was injected into the mixer co-axially while water was introduced peripherally. The visualization of the flow pattern was realized through a precise microscope, which can magnify the image up to 150 times of the original size. Several distinctive flow patterns, namely, dispersed bubbly flow, gas slug flow, liquid ring flow, liquid lump flow, annular flow, frothy or wispy annular flow, rivulet flow, liquid droplets flow were identified in their experiments. It is interesting to note that Rezkallah [1998] observed under microgravity conditions frothy slug-annular which is similar to the liquid ring flow. It has been confirmed that two-phase flow pattern are sensitive to the entrance conditions and the surface conditions of the inner wall of the test tubes.

For liquid-liquid two-fluid flow, Thorsen et al. [2001] performed a study in a system using tetradecane and water as the two working immiscible phase showed the existence of complex flow patterns. Their aim was to generate liquid droplets, whose size is controlled accurately. They showed that instability can develop as a competition between shear forces and surface tension in a microfluidic device. It was shown that self-assembly of the vesicles into patterns depends on channel geometry and relative fluid pressure, enabling

the production of motifs ranging from monodisperse droplets to helices and ribbons.

More recently, Dreyfus et al. [2003] visualized tetradecane microchannels. The channels are etched in glass, and covered by a silicon wafer, using anodic bonding. The cross section is $20 \times 200 \mu m$, and its length is $20 mm$. Similar as experiments by Thorsen et al. [2001], their study revealed the existence of a rich variety of patterns, depending on the flow-rates, and the injection configuration. The liquid ring (necklace) flow patterns were observed. The stratified flow pattern, which was not observed in water-gas two-phase experiments in microchannel, was observed in liquid-liquid experiments. Because the tetradecane was injected along the center line, the stratified flow showed the tetradecane in the central core and the water flow on the side; the interface between two fluids was a smooth circular ring. It turns out the water drops are easily formed than tetradecane drops in this particular experiment.

2.3 Liquid-liquid Two-layer Electroosmotic Flow

Brask et al. [2003] presented an electroosmotic pump design relying on two-liquid viscous drag to pump nonconducting liquid. A nonconducting liquid is dragged by a conducting liquid driven by electroosmotic flow. To realize this pump, they developed three new features that are essential for the design: pressure valves, reduced flow and optimized potential drop.

Watanabe et al. [2003] built an experiment rig to investigate the ion-drag pumping in a two-layer system: the water and an organic solvent. The solvent flowed by electroosmosis. Water flowed by the interfacial shear between the solvent and water layers. Because the electrodes are not in contact with the water, the problems such as the electrochemical decomposition of the solute, the generation of gases and the fluctuation of the pH of the solution can be avoided. But it is lack the theoretical analysis.

2.4 Numerical Methods for Simulation of Two-phase Flow

The numerical simulation of flows with interfaces is an interesting topic with a widespread applications, such as droplet, spray and combustion [Scardovelli and Zaleski, 1999]. A major difficulty is risen from the interface because the interface is subject to a number of physical phenomena. For example, the thickness of the interface is much smaller than the characteristic length of the flows and thus quantities are singular at the interface. Moreover, the interface will change in the topology with the flows. In recent years, a number of methods have been developed. These methods can be divided into two main classes depending on the type of grids used, moving or fixed, in the bulk of the phase. [Hyman, 1984; Scardovelli and Zaleski, 1999; Unverdi and Trayggvason, 1992].

In the full Lagrangian algorithms, the mesh moves together with the fluids [Cuenot et al., 1997; Magnaudet et al., 1995]. When the grid points move simply in a Lagrangian system, the grid may deform considerably. This is called the moving-grid method, which evolves frequent, tedious remeshing and rezoning. Hence, the moving-grid method is suitable to simulate simple two-fluid flow problem without significant topological changes of the interface. Whereas the fixed-grid method is used to solve the Navier-Stokes equation for the fluid flow, the interface is captured implicitly in the Eulerian approach or tracked explicitly in the Lagrangian approach.

There are many types of *interface capturing methods*, which can be classified according to their approach used. The volume of fluid (VOF) method [Gueyffier et al., 1999; Hirt and Nichols, 1981; Saurel and Abgrall, 1999; Welch and J., 2000] and level set method (LSM) [Chang et al., 1996; Sussman et al., 1994, 1998] are very popular for capturing interfaces using the fixed-grid method. The interface is not described explicitly, but is captured implicitly by an indicator function. It is normally the volume fraction of one fluid for VOF and the distance to the interface for LSM. This indicator function is advected with the fluids in the Eulerian approach. The interface is reconstructed from

this indicator function by some techniques [Osher and Fedkiw, 2001; Rider and Kothey, 1998].

There are also several algorithms, which use Lagrangian approaches to track the interface. Besides the static Eulerian grid, it uses massless particles scattered over the fluids. *Interface tracking methods* can be dividend into two categories, *front-tracking method* [Glimm et al., 1988; Tryggvason et al., 2001; Unverdi and Trayggvason, 1992] and *volume-tracking method* [Lafaurie et al., 1994; Rudman, 1997; Tome and McKee, 1994] . Surface marker method uses marker particles only on the interfaces. Volume marker method has markers/particles in the entire domain. It is well known that the marker-and-cell (MAC) [Amsden and Hanow, 1970; Chen et al., 1997; Tome and McKee, 1994] is a type of the volume-tracking method. Markers particles are inserted to identify the spatial region occupied by one phase. If a cell contains a particle it is considered to contain fluid, thus providing the interface. In the front-tracking methods the massless points are located only on the interface and are linked together in the mesh to present the interface, which moves together with the liquids. The tracking methods offer the most explicit way for the interface description.

There were works reported on a mixed of the above-mentioned methods. Sussman [2003] used a second-order coupled level set and volume-of-fluid method to simulate the movement of vapor bubbles. Aulisa et al. [2003] presented a new mixed markers and volume-of-fluid algorithm for reconstruction and advection of interfaces. Enright et al. [2002] used the marker particles method to rebuild the level set function to improve the mass conservation properties.

The capturing method is capable of computing highly complex geometric properties. The moving boundary can lead to corners and cups. Moreover, these methods allow for merging and breaking of the interface automatically [Osher and Fedkiw, 2002; Sethian, 2001]. However, these methods don't work well in the cases with front discontinuity. Normal and curvature computations need to be performed accurately on the interface. The curvature κ is ill-defined and arbitrarily large in the implicit methods. Furthermore,

relatively fine grids are required as long as the fluid interface is smooth. This increases the computational task.

The surface tension, especially in microchannels, effects are usually large compared with viscous damping. Since it is a singular term, the representation of surface tension creates the most obvious difficulties, even the curvatures are well found. The effect of surface tension leads to the existence of the so-called spurious currents [Lafaurie et al., 1994]. The presence of the surface charges in electrokinetic phenomena complicates this problem. The effects of the surface charge is difficult to implemented in the traditional way.

Chapter 3

Conservation Equations

3.1 Intrinsic Definition of Interface

Consider a system of two immiscible liquids, liquid 1 and liquid 2 as shown in Fig. 3.1. The two liquids are separated by a moving interfacial region. In most cases the surfaces in the interfacial region are assumed to be a parallel structure. Because the thickness of the interfacial layer is small compared to the mean curvature of the surface, the interfacial layer is replaced by a discontinuous sharp interface. An intrinsic definition of the surface is

$$F(\mathbf{r}, t) = 0 \quad (3.1)$$

in Cartesian coordinates. The function F is assumed to be defined, continuous and differentiable.

By this description of interface, only the normal velocity of the surface is well defined

$$w_{\perp}^s = -\frac{\partial F / \partial t}{|\nabla F|} \quad (3.2)$$

This velocity corresponds to the movement of the geometric surface. Other (tangential) velocity at the surface cannot be well defined by this description of interface.

By this approach, the time dependent surface is defined by $F(\mathbf{r}, t) = 0$, such that

Figure 3.1: Two-liquid system and the control volume including an interface, Γ

$F(\mathbf{r}, t) > 0$ refers to the points in one liquid and $F(\mathbf{r}, t) < 0$ to another liquid. This approach is also normally used in some theoretical development [Albano et al., 1979; Kovac, 1977] and numerical simulations about surfaces [Osher and Fedkiw, 2001; Unverdi and Trayggvason, 1992].

In this dissertation, we consider one liquid is aqueous liquid and another is a non-aqueous liquid. There will be high capacitance charged region of ions, termed electrical double layer (EDL) formed on the aqueous liquid side. When an external electric field is applied, the presence of the net charges in the EDL region induces a body force. Outside the interfacial region, the conservation equations are valid. The governing equations in the bulk will be given next. Then the electrokinetic phenomena are presented. The conservation equations for the interface will be given in Chapter 4.

3.2 Bulk Conservation Equations

Consider a control volume, $\mathcal{V}$, with boundary, $\partial\mathcal{V}$ in a continuum. For any property, θ , the evolution of which satisfies the following conservation equation [de Groot and Mazur, 1984]

$$\frac{\partial(\rho\theta)}{\partial t} + \nabla \cdot [\mathbf{J} + \rho\theta\mathbf{v}] = \rho\dot{\theta} \quad (3.3)$$

where ρ is the density, $\mathbf{v}$ is the velocity of the continuum, $\mathbf{J}$ is the transport flux, $\mathbf{n}$ is the outward unit normal to the boundary of $\partial\mathcal{V}$ and $\rho\dot{\theta}$ is the volumetric production of the property. The detailed derivation of this general equation is shown in Appendix A. With this general equation one can write down the conservation laws for mass, momentum and energy of the two liquids within a microchannel.

3.2.1 Continuity equation

For conservation of mass, the property is taken as $\psi = 1$, the flux $\mathbf{J} = 0$ and the mass production $\dot{\psi} = 0$. The Eq. (3.3) becomes

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0 \quad (3.4)$$

This is the equation of continuity. For an incompressible Newtonian fluid, the continuity equation becomes

$$\nabla \cdot \mathbf{v} = 0 \quad (3.5)$$

3.2.2 Momentum equation of the two liquids

Non-aqueous solution

For the non-aqueous solution, one has: $\psi = \mathbf{v}$, $\dot{\psi} = \mathbf{f}$ and $\mathbf{J} = -\mathbf{T}$, where $\mathbf{f}$ is the body force, $\mathbf{T}$ is the stress tensor (incompressible liquid) [White, 1991, p. 67]

$$T_{ij} = -p\delta_{ij} + \mu \left(\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} \right) \quad (3.6)$$

where μ is the viscosity. Thus the bulk conservation equation for momentum is the Navier-Stocks equation as

$$\frac{\partial(\rho \mathbf{v})}{\partial t} + \nabla \cdot (\rho \mathbf{v} \mathbf{v}) = \nabla \cdot \mathbf{T} + \rho \mathbf{f} \quad (3.7)$$

Aqueous liquid

In the aqueous liquid, electrostatic phenomena and hydrodynamics are coupled by the Maxwell's stress tensor. In a dielectric medium without magnetic contribution, the Maxwell's stress tensor is expressed as [Landau et al., 1984, p. 61],

$$\mathbf{T}^M = \epsilon_r \epsilon_0 \mathbf{E} \mathbf{E} - \frac{1}{2} \epsilon_r \epsilon_0 \left[1 - \frac{\rho}{\epsilon_r} \left(\frac{\partial \epsilon_r}{\partial \rho} \right)_T \right] (\mathbf{E} \cdot \mathbf{E}) \mathbf{I} \quad (3.8)$$

where ϵ_r and $\epsilon_0 = 8.85 \times 10^{-12} \text{C}/(\text{N} \cdot \text{m}^2)$ is the relative permittivity and the vacuum permittivity, respectively. Here, $\mathbf{E} = -\nabla \Phi$ is the electric field strength, where Φ is the electrostatic potential. $(\partial \epsilon_r / \partial \rho)_T$ is the change in relative permittivity with density at constant temperature.

For the balance law of momentum, the current $\mathbf{J} = -\mathbf{T}$ is replaced by $\mathbf{J} = -\mathbf{T} - \mathbf{T}^M$. The bulk balance law for momentum, Eq. (3.7), is replaced by

$$\frac{\partial(\rho \mathbf{v})}{\partial t} + \nabla \cdot (\rho \mathbf{v} \mathbf{v}) = \nabla \cdot (\mathbf{T} + \mathbf{T}^M) + \rho \mathbf{f} \quad (3.9)$$

For an incompressible liquid, expanding the Maxwell stress tensor and the stress tensor for incompressible Newtonian liquids yields

$$\rho \frac{d\mathbf{v}}{dt} = -\nabla \left[p - \frac{1}{2} \epsilon_0 \rho \left(\frac{\partial \epsilon}{\partial \rho} \right)_T \mathbf{E} \cdot \mathbf{E} \right] - \frac{1}{2} \epsilon_0 \mathbf{E} \cdot \mathbf{E} \nabla \epsilon + \rho_q \mathbf{E} + \mu \nabla^2 \mathbf{v} \quad (3.10)$$

In this equation, the presence of the nonhomogeneous dielectric permeability and net volume charges works as a body force for liquids. To simplify, we consider constant permeability in the whole fluid dielectric. Eq. (3.10) reduces

$$\rho \frac{D\mathbf{v}}{Dt} = -\nabla p + \rho_q \mathbf{E} + \mu \nabla^2 \mathbf{v} \quad (3.11)$$

3.3 Electric Double Layer

Most surface (including solid surfaces and interfaces between immiscible liquids) spontaneously acquire a surface electric charge when brought into contact with polar solutions[Probstein, 1994]. This surface charge will effect the charge distribution near the surface. Ions of opposite charge to that of the surface (counterions) are attracted to the surface while the ions of same charge (coions) are repelled from the surface. This attraction and repulsion result in the formation of the *electric double layer* (EDL), in which there is an excess of counterions over coions. The number of net charge in the EDL region should be equal to those at the surface to keep neutrality.

Figure 3.2: Schematic structure of electric double layer and representation of a possible potential distribution, after Probstein [1994, p.190].

In current theories of electric double layer, the structure of EDL on the solution side is considered consisting of two parts: compact/inner layer and diffuse layer [Hunter, 1988, p. 34]. The ions in the inner layer are considered to be immobile as counterions are strongly attracted to the charged surface. This compact layer is usually about several Angstroms thick, defined as δ in Fig. 3.2. Ions in the diffuse layer are mobile resulting from the random thermal motion as they are less attracted by the electrostatic interaction. The thickness of the diffuse layer, λ_D is dependent on the bulk ions concentration and electrical properties of the solution, usually ranging from several nanometers to the order of microns. The plane separating the compact layer and diffuse layer is called Stern plane. As shown in Fig. 3.2 [Shaw, 1992, p. 183], the potential at this plane, Φ_δ , is close to the *zeta potential* (ζ potential), which is defined as the potential at the *shear plane* [Hunter, 1988, p. 216]. The shear plane is an imaginary surface and somewhat arbitrary but characterized as the plane at which the mobile portion of the diffuse layer can ‘slip’ or flow past the charged surface [Probstein, 1994, p. 193].

When the mobile portion of the diffuse layer and an external electric field interact in the viscous shear layer near the charged surface, *electrokinetic phenomena* arise. The four electrokinetic phenomena following the description of Shaw [1992, p. 190] are

1. *Electrophoresis* — the movement of a charged surface plus attached material (i.e. dissolved or suspended material) relative to stationary liquid by an applied electric field.
2. *Electroosmosis* — the movement of liquid relative to a stationary charged surface (e.g. a capillary or porous plug) by an applied electric field (i.e. the complement of electrophoresis). The pressure necessary to counterbalance electroosmotic flow is termed the *electroosmotic pressure*.
3. *Streaming potential* — the electric field created when liquid is made to flow along a stationary charged surface (i.e. the opposite of electroosmosis).

4. *Sedimentation potential* — the electric field created when charged particles move relative to stationary liquid (i.e. the opposite of electrophoresis).

3.4 Electric Potential and Species

By scale analysis, the characteristic time for electric phenomena is much larger than the one for magnetic phenomena. Therefore, when the external magnetic field is absent, magnetic effects can be ignored compared with electric effects [Saville, 1997]. Accordingly, in the phenomenological theory of diffuse charge in dilute electrochemical systems, the electrostatic potential, ψ , obeys Poisson's equation,

$$\nabla^2 \psi = -\frac{\rho_q}{\epsilon} \quad (3.12)$$

where $\epsilon = \epsilon_r \epsilon_0$. Eq. (3.12) shows how the field is altered by the presence of free charges. In liquids, charge is carried by ions, so species conservation equations must be included to complete the description. Free charge density and ion concentration are related as

$$\rho_q = e \sum_k z_k n_k \quad (\text{Cm}^{-3}) \quad (3.13)$$

Here e is the charge on a proton and z_k is the valence of the k^{th} species whose concentration is n_k . Note that the species may be electrically neutral, that is $\sum_k z_k = 0$.

Based on the assumption of thermodynamic equilibrium, for a symmetric electrolyte ($\zeta_+ = \zeta_- = \zeta_0$ e.g. KCl), the concentration of ions in the EDL region follows the Boltzmann distribution [Hunter, 1988, p. 23]

$$n_1 = n_0 \exp(-z_0 e \psi / k_b T) \quad \text{and} \quad n_2 = n_0 \exp(z_0 e \psi / k_b T) \quad (3.14)$$

This means that the local system is at thermodynamic equilibrium, where the electrical and diffusional forces on the charges are balanced. Thus, from Eq. (3.13), the net

volume charge density is

$$\rho_q = -2z_0en_0 \sinh(z_0e\psi/k_bT) \quad (3.15)$$

Therefore, Eq. (3.12) becomes

$$\nabla^2\psi = \frac{2z_0en_0}{\epsilon} \sinh\left(\frac{z_0e\psi}{k_bT}\right) \quad (3.16)$$

This is the famous Poisson-Boltzmann equation.

3.5 Interfacial Conservation Equations

To obtain the boundary conditions or coupling conditions at the interface, interfacial conservation equation should be defined properly inside the control volume including the interface. Because the thickness of the interfacial layer is small compared to the mean curvature of the macroscopic surface, the interfacial layer is replaced by a sharp interface where interface quantities are defined by integration over the thickness of the layer [Gatignol and Prud'homme, 2001; Ishii, 1975]. Jump conditions through the interface are derived from the interfacial conservation equations [Bedeaux et al., 1976; Kovac, 1977; Scriven, 1960; Slattery, 1990].

For the control volume including an interface in Fig. 3.1, the interfacial conservation for any interfacial quantity, θ^s , has been developed by Gatignol and Prud'homme [2001]

$$\rho^s \frac{d_{\mathbf{v}^s} \theta^s}{dt} + [[\mathbf{J} \cdot \mathbf{n} + \dot{m}(\theta - \theta^s)]] + \nabla_s \cdot \mathbf{J}_{||}^s = \rho^s \dot{\theta}^s \quad (3.17)$$

Here, ρ^s is the interfacial mass density, $\mathbf{w}^s$ is the control velocity. The notation $[[\theta]] = \theta_2 - \theta_1$ is the jump quantity between the two values of ϕ taken respectively on the boundaries of the interfacial layer. $\dot{m}$ is the mass flux across the interface. The notation ∇_s corresponds to the tangential gradient operator along the surface and $\mathbf{J}_{||}^s$, which is

the interfacial transport flux. $\dot{\theta}^s$ is the interfacial generation of θ^s . This is the general equation for transport phenomena of an interfacial layer. In the following, we will derive the interfacial conservation equations for momentum with electric effects from Eq. (3.17).

For the interface including electric charges, we have: $\psi^s = \mathbf{v}^s \cdot \mathbf{J} = -\mathbf{T} - \mathbf{T}^M$ and $\mathbf{J}_\parallel^s = -\mathbf{T}_\parallel^s$. That $\mathbf{J}_\parallel^s = -\mathbf{T}_\parallel^s$ means that the electric field is not singular, though discontinuous, at the interface [Wolff and Albano, 1979]. Substituting them into Eq. (3.17) yields

$$\rho^s \frac{d\mathbf{v}^s}{dt} + [[\dot{m}(\mathbf{v} - \mathbf{v}^s) - (\mathbf{T} + \mathbf{T}^M) \cdot \mathbf{n}]] - \nabla_s \cdot \mathbf{T}_\parallel^s = \rho_a \mathbf{f}^s \quad (3.18)$$

$\mathbf{T}_\parallel^s$ is the interface stress tensor. Ignoring the surface dilatational viscosity and surface shear viscosity, the interfacial stress tensor is defined as reported by [Slattery, 1990, p. 193]

$$\mathbf{T}_\parallel^s = \sigma(\mathbf{I} - \mathbf{nn}) \quad (3.19)$$

where σ is the surface tension. Here we consider a simple situation, capillary surface without mass, $\rho^s = 0$ and $\mathbf{f}^s = 0$. Moreover, there is no mass flow rate through the capillary surface ($\dot{m} = 0$). Then Eq. (3.18) reduces into

$$[[\mathbf{T} + \mathbf{T}^M]] \cdot \mathbf{n} + \nabla_s \cdot [\sigma(\mathbf{I} - \mathbf{nn})] = 0 \quad (3.20)$$

The pressure stress tensor, defined in Eq. (3.6), is rewritten as

$$\mathbf{T} = -p\mathbf{I} + \mathbf{T}' \quad (3.21)$$

where $\mathbf{T}' = \mu(\nabla\mathbf{v} + \nabla\mathbf{v}^T)$ is the viscosity stress tensor. Hence, Eq. (3.20) is rewritten as

$$- [[\mathbf{T}' \cdot \mathbf{n} + \mathbf{T}^M \cdot \mathbf{n}]] + [[p]] \mathbf{n} - \nabla_s \cdot [\sigma(\mathbf{I} - \mathbf{nn})] = 0 \quad (3.22)$$

We also have

$$\nabla_s \cdot [\sigma(\mathbf{I} - \mathbf{nn})] = \nabla_s \sigma - \sigma(\nabla \cdot \mathbf{n})\mathbf{n} \quad (3.23)$$

Therefore, we obtain the desired stress balance at any part on an interface,

$$- [[\mathbf{T}' \cdot \mathbf{n}]] + [[p]] \mathbf{n} - [[\mathbf{T}^M]] \cdot \mathbf{n} - \nabla_s \cdot [\sigma(\mathbf{I} - \mathbf{nn})] = 0 \quad (3.24)$$

At boundaries, the tangential components of the electric field strength, $\mathbf{E}$, are continuous and the normal component jumps as

$$[[\epsilon \mathbf{E}]] \cdot \mathbf{n} = \rho_q^s \quad (3.25)$$

where ρ_q^s is the interfacial charge density (free charge per unit area). This equation can be further projected onto the normal and tangential directions as

$$\begin{aligned} [[(\mathbf{n} \cdot \mathbf{T}^M) \cdot \mathbf{n}]] &= \frac{1}{2} [[\epsilon \epsilon_0 (\mathbf{E} \cdot \mathbf{n})^2 - \epsilon \epsilon_0 (\mathbf{E} \cdot \mathbf{t}_1)^2 - \epsilon \epsilon_0 (\mathbf{E} \cdot \mathbf{t}_2)^2]] \\ &= \frac{1}{2} \rho_q^s [[\mathbf{E}^+ + \mathbf{E}^-]] \\ &= \rho_q^s [[\mathbf{E}]]_+ \cdot \mathbf{n} \end{aligned} \quad (3.26a)$$

$$[[[(\mathbf{n} \cdot \mathbf{T}^M) \cdot (\mathbf{I} - \mathbf{nn})]] \cdot \mathbf{t}_i] = \rho_q^s \mathbf{E} \cdot (\mathbf{I} - \mathbf{nn}) \quad (3.26b)$$

because the tangential components of $\mathbf{E}$ are continuous. The notation $[[\mathbf{E}]]_+ = \frac{1}{2}(\mathbf{E}_1 + \mathbf{E}_2)$

Using Eqs. (3.26), projections of Eq. (3.24) in normal and tangential directions are, respectively

$$[[p]] = \kappa \sigma + [[T']] : \mathbf{nn} + \rho_q^s [[\mathbf{E}]]_+ \cdot \mathbf{n} \quad (3.27a)$$

$$\nabla_s \sigma + \mathbf{n} \cdot [[\mathbf{T}']] \cdot (\mathbf{I} - \mathbf{nn}) - \rho_q^s \mathbf{E} \cdot (\mathbf{I} - \mathbf{nn}) = 0 \quad (3.27b)$$

3.6 Dimensionless Equations

In the previous section, the governing equation for potential in 1-1 electrolyte and the Navier-Stokes equation are

$$\nabla^2 \psi = \frac{2z_0 e n_0}{\epsilon} \sinh\left(\frac{z_0 e \psi}{k_b T}\right) \quad (3.28a)$$

$$\rho_q = -2z_0 e n_0 \sinh(z_0 e \psi / k_b T) \quad (3.28b)$$

$$\nabla \cdot \mathbf{v} = 0 \quad (3.28c)$$

$$\frac{\partial(\rho \mathbf{v})}{\partial t} + \nabla \cdot (\rho \mathbf{v} \mathbf{v}) = -\nabla p + \rho_q \mathbf{E} + \mu \nabla^2 \mathbf{v} \quad (3.28d)$$

Define reference parameters L_{ref} and V_{ref} for the length and the velocity scale, respectively, above equations are normalized by

$$\mathbf{r} = L_{\text{ref}} \bar{\mathbf{r}} \quad t = \frac{L_{\text{ref}}}{U_{\text{ref}}} \bar{t} \quad (3.29a)$$

$$\mathbf{v} = V_{\text{ref}} \bar{\mathbf{v}} \quad p = \bar{p} \rho_{\text{ref}} V_{\text{ref}}^2 \quad (3.29b)$$

$$n_i = n_0 \bar{n}_i \quad \psi = \frac{k_b T}{z_0 e} \bar{\psi} \quad (3.29c)$$

$$\rho = \rho_{\text{ref}} \bar{\rho} \quad \mu = \mu_{\text{ref}} \bar{\mu} \quad (3.29d)$$

$$\rho_q = 2z_0 e n_0 \bar{\rho}_q \quad (3.29e)$$

The Eqs. (3.28) are normalized as

$$\nabla^2 \bar{\psi} = K^2 \sinh(\bar{\psi}) \quad (3.30a)$$

$$\bar{\rho}_q = -\bar{\psi} \quad (3.30b)$$

$$\nabla \cdot \bar{\mathbf{v}} = 0 \quad (3.30c)$$

$$\frac{\partial(\bar{\rho}\bar{\mathbf{v}})}{\partial t} + \nabla \cdot (\bar{\rho}\bar{\mathbf{v}}\bar{\mathbf{v}}) = -\nabla\bar{p} + \mathbf{G}\bar{\rho}_q + \frac{1}{\text{Re}}\bar{\mu}\nabla^2\bar{\mathbf{v}} \quad (3.30d)$$

where

$$K = \kappa L_{\text{ref}}, \quad \kappa = \left(\frac{2z_0^2 e^2 n_0}{\epsilon k_b T} \right)^{1/2},$$

$$\mathbf{G} = \frac{2n_0 z_0 e L_{\text{ref}} \mathbf{E}}{\rho_{\text{ref}} V_{\text{ref}}^2} \quad \text{and} \quad \text{Re} = \frac{\rho_{\text{ref}} V_{\text{ref}} L_{\text{ref}}}{\mu_{\text{ref}}} \quad (3.31)$$

Dimensionless boundary conditions for electric potential

At the surface or interface hold certain charge densities, ρ_q^s , the tangential components are continuous and the normal component is:

$$[[\nabla\bar{\psi}(\Gamma)]] \cdot \mathbf{n}(\Gamma) = -\frac{\rho_q^s z_0 e L_{\text{ref}}}{\epsilon k_b T} = \bar{\rho}_q^s \quad (3.32a)$$

At somewhere it is equal to the surface zeta potential:

$$\bar{\psi} = \bar{\zeta}_s \quad (3.32b)$$

Dimensionless boundary conditions for flow

At the solid wall surface:

$$\bar{\mathbf{v}} = 0 \quad (3.33a)$$

or symmetric conditions according to special cases

$$\frac{\partial\bar{\mathbf{v}}}{\partial n} = 0 \quad (3.33b)$$

.

Chapter 4

Analytical Analysis

Within the diffuse layer, the net charge density, ρ_q , is not zero. If an electric field is applied tangentially along a charged surface, the electric field will exert a body force on the charges in the diffuse layer. This movement of charges, under the influence of applied electrical field, will pull the surrounding fluid with them, resulting in the electroosmotic flow (EOF). To induce electroosmosis, however, the working liquid is required to be a polar liquid with significant electrical conductivity which is called aqueous solution. Non-aqueous liquids such as oil cannot generate EOF.

Figure 4.1: Schematic of the phenomenon and coordinate system

The system which will be considered is shown in Fig. 4.1, consisting of an aqueous solution and a non-aqueous liquid. EDLs form near the channel walls contacted with the aqueous solution and the liquid-liquid interface. When an external electric field is applied parallel to the channel walls, the aqueous solution flows along the x axis, resulting in the electroosmotic flow. The non-aqueous fluid is dragged by the viscous force at the interface.

An obvious difference between liquid-liquid interfaces from those of the liquid-wall is that the interfaces between the two liquids are not stationary. The external electric intensity interacts with the free charges at the interface to generate a surface force. Because the solid wall remains stationary, this force is ignored in the analysis of single-fluid electroosmotic flow. For the two-liquid electroosmotic system, however, this surface force is significant and has to be taken into account.

In this chapter, the interface between the two liquids is described as a dividing surface, which has the 'excess' surface charge density. The analytical solution of this electroosmotic flow is obtained under some assumptions.

4.1 Electrical Double Layer Potential

4.1.1 Linearization and solution

To analyze this system, a Cartesian orthogonal coordinate system (x, y, z) is used where the origin, O , is at the intersection of the interface and the symmetric line as shown in Fig. 4.1. A planar interface is assumed which is satisfied when contact angle is close to 90° or the Bond number is large. This assumption strictly limits the application of this model. The heights of the aqueous solution and the non-aqueous liquid are denoted by h_1 and h_2 , respectively. Half of the width of the channel is denoted by w . The aspect ratio is defined as $\chi = h/(2w)$ of the height of the microchannel to its width. EDLs form near the liquid-liquid interface and the channel wall that is in contact with the aqueous

solution. Because the bottom wall and the side wall may be made of different materials, we specify that the zeta potential at the bottom wall is ζ_1 and at the side wall is ζ_2 ; and the zeta potential at the interface is ζ_3 . The electroosmotic flow is along the x direction. Due to symmetry, only half of the cross section of the rectangular channel is considered.

Generally speaking, the non-linear Poisson-Boltzmann Eq. (3.30a) cannot be solved analytically. But for small potential of $0 < \bar{\psi} < 1$, the right hand side of Eq. (3.30a) can be mathematically approximated as $K \sinh(\bar{\psi}) \approx K\bar{\psi}$ [Keh and Tseng, 2001; Probst, 1994]. This approximation is termed as the *Debye-Hückel* approximation. Therefore in the rectangular channel as shown in Fig. 4.1, Eq. (3.30a) can be written in the linear form as,

$$\frac{\partial^2 \bar{\psi}}{\partial \bar{z}^2} + \frac{\partial^2 \bar{\psi}}{\partial \bar{y}^2} = K^2 \bar{\psi} \quad (4.1)$$

In the aqueous solution, the electrical potential equals the wall zeta potential at the channel wall and the interface zeta potential at the interface. Due to the symmetry of the EDL field in the rectangular channel, Eq. (4.1), is subjected to the following boundary conditions,

$$\begin{cases} \partial \bar{\psi} / \partial \bar{z} = 0 & \text{at } \bar{z} = 0 \\ \bar{\psi} = \bar{\zeta}_2 & \text{at } \bar{z} = w/L_{\text{ref}} = \bar{w} \\ \bar{\psi} = \bar{\zeta}_3 & \text{at } \bar{y} = 0 \\ \bar{\psi} = \bar{\zeta}_1 & \text{at } \bar{y} = -h_1/L_{\text{ref}} = \bar{h}_1 \end{cases} \quad (4.2)$$

where the zeta potentials are non-dimensionalized by $(k_b T)/(z_0 e)$. Using the separation of variables method, the analytical solution of Eq. (4.1) with the boundary conditions,

(4.2), is obtained as

$$\begin{aligned} \bar{\psi}(\bar{z}, \bar{y}) = \sum_{j=0}^{\infty} &= \frac{4(-1)^{j+1} [\bar{\zeta}_1 \sinh(B_j \bar{y}) + \bar{\zeta}_3 \sinh(B_j \bar{h}_1 - B_j \bar{y})] \cos(\lambda_j \bar{z})}{(2j-1)\pi \sinh(B_j h_1)} \\ &+ \sum_{p=1}^{\infty} \frac{2\bar{\zeta}_2 [1 + (-1)^{p+1}] \cosh(A_p \bar{z})}{p\pi \cosh(A_p \bar{w})} \sin\left(\frac{p\pi}{\bar{h}_1} \bar{y}\right) \end{aligned} \quad (4.3)$$

where

$$\begin{cases} A_p = \sqrt{K^2 + \frac{p^2 \pi^2}{\bar{h}_1^2}} \\ B_j = \sqrt{K^2 + \frac{(2j-1)^2 \pi^2}{4\bar{w}^2}} \\ \lambda_j = \frac{(2j-1)\pi}{2\bar{w}} \end{cases} \quad (4.4)$$

In the above discussion of electroosmosis, the charge state of the surface is described in terms of surface potential at the shear plane, which is in turn identified with the zeta potential in Probstein [1994, p. 212]. This surface potential is related to certain charge density at the surface by Eq. (3.32). From electrostatics, the normal component of the gradient of the electric potential, ψ , jumps by an amount proportional to the surface charge density, ρ_q^s . That is,

$$\rho_q^s = -\epsilon \frac{\partial \psi}{\partial y} \quad (4.5)$$

It is assumed that the gradient of electric potential in the non-aqueous liquid vanishes. Using the reference surface charge density as $(\epsilon k_b T)/(L_{\text{ref}} z_0 e)$, one obtained the dimensionless surface charge density at the two-liquid interface as

$$\begin{aligned} \bar{\rho}_q^s(\bar{z}) = -\frac{\partial \bar{\psi}(\bar{z}, 0)}{\partial \bar{y}} &= \sum_{j=1}^{\infty} \frac{4(-1)^{j+1} B_j}{(2j-1)\pi} \left[\frac{\bar{\zeta}_3}{\tanh(B_j \bar{h}_1)} - \frac{\bar{\zeta}_1}{\sinh(B_j \bar{h}_1)} \right] \cos(\lambda_j \bar{z}) \\ &- \sum_{p=1}^{\infty} \frac{2\bar{\zeta}_2 [(-1)^{p+1} + 1] \cosh(A_p \bar{z})}{\bar{h}_1 \cosh(A_p \bar{w})} \end{aligned} \quad (4.6)$$

It should be mentioned that the surface charge at the interface, ρ_q^s , is opposite in sign to the volumetric net charge in the EDL region at the vicinity of the interface. From Eq.

(4.5), the surface charge density at the bottom wall, ρ_{qw1}^s , and the side wall, ρ_{qw2}^s , can be obtained. Here, for a large value of EDL parameter, K , (thin EDL), electroneutrality condition is hold,

$$\int_0^w [\rho_q^s(z) + \rho_{qw1}^s(z) dz] + \int_{-h_1}^0 \rho_{qw2}^s(y) dy + \int_0^w \int_{-h_1}^0 \rho_q(z, y) dz dy = 0 \quad (4.7)$$

This has been shown in Hunter [1988, p. 37].

From the solution of Eq. (4.6), it can be seen that the contribution of zeta potential at the bottom wall, ζ_1 , is relatively small and the contribution of the side wall, ζ_2 , is also relatively small except when z approaches w . Once the electric potential distribution is known, the volumetric net charge density from Eq. (3.15) can be also linearized as

$$\bar{\rho}_q \approx -\bar{\psi}(\bar{z}, \bar{y}) \quad (4.8)$$

This volumetric net charge density, Eq. (4.8), and the above interface charge density, Eq. (4.6), are required to determine the electrostatic force caused by the presence of zeta potential. The bulk electrostatic force is considered as an additional body force exerting on the aqueous solution to modify the conventional Navier-Stokes equation. The non-aqueous liquid is dragged by the viscous forces from the aqueous solution and the external electrostatic force due to the electrokinetic charge density at the interface, which will be discussed in the following.

4.1.2 Electrical potential distribution in the aqueous solution

In the analysis, an aqueous binary electrolyte, KCl, with univalent charges is used as the aqueous solution. The dimension of microchannel is $40\mu\text{m}$ width and $40\mu\text{m}$ height. The aqueous solution holds the lower half of the channel and the lower EO mobility liquid holds the upper half. The height of the aqueous solution, h_1 , and the non-aqueous liquid, h_2 , are both at $20\mu\text{m}$. The characteristic length L_{ref} is equal to the

(a) $\zeta_3 = \zeta_1$

(b) $\zeta_3 = 0.5\zeta_1$

(c) $\zeta_3 = 0$

Figure 4.2: Electrical potential distributions.

height of the channel. Also when results are presented in the following, the origin, O , is moved to the intersection of the bottom wall and the symmetric line. Therefore, the dimensionless value of y , $\bar{y}$, increase from 0 to 1. The half of the width is $w = 20\mu\text{m}$. The normalized zeta potential at the wall depends on ionic valence and concentration of the electrolyte and the material properties of the wall [Erickson et al., 2000]. Here we use $\zeta_{\text{ref}} = 25.7\text{mV}$. The zeta potential between the two immiscible liquids not only depends on the ionic properties of the two liquids, but it also depends on the pH values, and it can also change its polarity when surfactant is present [Gu and Li, 1997]. We choose the wall zeta potentials to be the same at $\zeta_1 = \zeta_2 = -25\text{mV}$ as the default value.

The zeta potential at surfaces and non-dimensional parameter K are presented to evaluate parameters affecting the EDL profiles, which is defined as $K = \kappa L_{\text{ref}}$. The concentration of the aqueous solution is chosen in the range from 10^{-7}M , 10^{-6}M and 10^{-5}M , corresponding to the value of K is 41.2 ($1/\kappa \approx 970\text{nm}$), 130 ($1/\kappa \approx 307\text{nm}$) and 412 ($1/\kappa \approx 97\text{nm}$), respectively. Fig. 4.2 shows the results of Eq. (4.3) with different values of K along the symmetrical line. The EDL only exists in the aqueous solution. Zeta potentials depend on the ionic properties of the solution and the material properties of surfaces. Normally a lower concentration corresponds to a higher zeta potential. However, because there is no reliable information on the zeta potential at the liquid-liquid interface (ζ_3), we consider three different cases and these are: the interfacial zeta potential is the same as the wall zeta potential, it is half of the wall zeta potential and zero. The interfacial zeta potential affects the electrical potential dramatically. The existence of interfacial zeta potential induces an EDL near the liquid-liquid interface, where the electroosmotic body forces are present. From Fig. 4.2, it can be seen that the value of K determines the EDL thickness: small value of K corresponds to a thick EDL; and large value of K to a very thin EDL. A lower concentration and a larger channel size result in a larger value of K , and hence a thinner EDL.

4.2 Momentum Equations of Two-liquid Flow

The dimensionless equation of motion for an incompressible laminar liquid is given by Eq. (3.30d)

$$\frac{\partial(\bar{\rho}\bar{\mathbf{v}})}{\partial\bar{t}} + \nabla \cdot (\bar{\rho}\bar{\mathbf{v}}\bar{\mathbf{v}}) = -\nabla\bar{p} + \mathbf{G}\bar{\rho}_q + \frac{1}{\text{Re}}\bar{\mu}\nabla^2\bar{\mathbf{v}} \quad (3.30d)$$

To evaluate the electrokinetic effects, it is assumed that the flow is formed by two simple immiscible Newtonian liquids with constant viscosities, which are independent of shear rate and the local electric field strength. The flow is a transient, fully-developed, laminar stratified flow.

The main simplifying assumptions in the current analysis are as follow:

1. The two liquids are simple Newtonian incompressible liquids.
2. The liquids' properties are independent of local electric field and ion concentration.
The electric field strength and ion concentration may affect the properties of the conducting fluid. In the current study, we consider only dilute solutions and these effects are neglected [Dutta et al., 2002b].
3. The liquids' properties are independent of temperature. Joule heating is neglected for dilute electrolytes (e.g. the concentration $C < 10^{-3}\text{M}$) and low field strength (e.g. $E_x < 100\text{kV/m}$) [Tang et al., 2004].
4. The two-fluid flow is fully developed with no-slip boundary condition. Currently, we only consider the fully-developed section of the channel, which is away from the entrance and exit. The second term on the left hand of Eq. (3.30d), $\nabla \cdot (\bar{\rho}\bar{\mathbf{v}}\bar{\mathbf{v}})$, will be vanished.
5. Provided that the aspect ratio, $\chi = h/(2w)$, the height of the microchannel to its width is large, the pressure gradient at the fully developed region is considered as the same for two liquids.

As EDLs only form in the aqueous solution, the momentum equations of the two liquids reduce to

$$\frac{\partial \bar{u}_1}{\partial \bar{t}} = \frac{1}{\text{Re}} \left(\frac{\partial^2 \bar{u}_1}{\partial \bar{z}^2} + \frac{\partial^2 \bar{u}_1}{\partial \bar{y}^2} \right) + G_x \bar{\rho}_q(\bar{z}, \bar{y}) - \frac{d\bar{p}}{d\bar{x}} \quad \text{for the aqueous solution} \quad (4.9a)$$

and

$$\bar{\rho}_2 \frac{\partial \bar{u}_2}{\partial \bar{t}} = \bar{\mu}_2 \frac{1}{\text{Re}} \left(\frac{\partial^2 \bar{u}_2}{\partial \bar{z}^2} + \frac{\partial^2 \bar{u}_2}{\partial \bar{y}^2} \right) - \frac{d\bar{p}}{d\bar{x}} \quad \text{for the non-aqueous liquid} \quad (4.9b)$$

where $G_x = (2z_0 \epsilon n_0 L_{\text{ref}} E_x) / (\rho_{\text{ref}} U_{\text{ref}}^2)$. Here the reference viscosity and density are the ones of aqueous solution as $\mu_{\text{ref}} = \mu_1$ and $\rho_{\text{ref}} = \rho_1$. Thus, $\bar{\mu}_1 = 1$ and $\bar{\mu}_2 = \mu_2 / \mu_1$ is the dynamic viscosity ratio (β).

At the interface, matching conditions must be obeyed. In the fully-developed region, there are the continuity of the velocity

$$u_1 = u_2 \quad (4.10a)$$

and the shear stress balance from Eq. (3.27), which jumps abruptly at the interface because of the presence of a certain surface charge density,

$$\mu_1 \frac{\partial u_1}{\partial n} = \mu_2 \frac{\partial u_2}{\partial n} - E_x \rho_q^s \quad (4.10b)$$

Here n is the normal direction along the interface between the two liquids. In the problem, it is assume that the interface is flat. Therefore, the normal direction of interface is along y . The dimensionless matching conditions become

$$\begin{cases} \bar{u}_1(\bar{z}, 0, \bar{t}) = \bar{u}_2(\bar{z}, 0, \bar{t}) \\ \frac{\partial \bar{u}_1(\bar{z}, 0, \bar{t})}{\partial \bar{y}} = \beta \frac{\partial \bar{u}_2(\bar{z}, 0, \bar{t})}{\partial \bar{y}} - M \bar{\rho}_q^s(\bar{z}) \end{cases} \quad (4.11)$$

where $M = (\epsilon k_b T E_x) / (z_0 e U_{\text{ref}} \mu_{\text{ref}})$.

In the rectangular channel, the dimensionless boundary conditions for the aqueous solution are

$$\begin{cases} \partial \bar{u}_1 / \partial \bar{z} = 0 & \text{at } \bar{z} = 0 \\ \bar{u}_1 = 0 & \text{at } \bar{z} = \bar{w} \\ \bar{u}_1 = 0 & \text{at } \bar{y} = \bar{h}_1 \\ \bar{u}_1 = 0 & \text{when } \bar{t} = 0 \end{cases} \quad (4.12a)$$

The dimensionless boundary conditions for the non-aqueous liquid are

$$\begin{cases} \partial \bar{u}_1 / \partial \bar{z} = 0 & \text{at } \bar{z} = 0 \\ \bar{u}_2 = 0 & \text{at } \bar{z} = \bar{w} \\ \bar{u}_2 = 0 & \text{at } \bar{y} = \bar{h}_2 \\ \bar{u}_2 = 0 & \text{when } \bar{t} = 0 \end{cases} \quad (4.12b)$$

Because of linearity, the velocity of the aqueous solution in Eq. (4.9a) can be decomposed into two parts

$$\bar{u}_1 = \bar{u}_1^E + \bar{u}_1^P \quad (4.13a)$$

where $\bar{u}_1^E$ corresponds to the velocity component driven by the electroosmotic forces and $\bar{u}_1^P$ corresponds to the velocity component by the pressure gradient. Consequently, the velocity of the non-aqueous is decomposed as

$$\bar{u}_2 = \bar{u}_2^E + \bar{u}_2^P \quad (4.13b)$$

where $\bar{u}_2^E$ corresponds to the velocity component influenced by the electroosmotic flow of the aqueous solution and $\bar{u}_1^P$ corresponds to the velocity component by the pressure gradient.

The holdup of the aqueous solution, ε , is defined as the ratio of the area occupied by the aqueous solution to the whole area of the section of the channel. In this problem,

because of planer interface it is simply given as

$$\varepsilon = \frac{|\bar{h}_1|}{|\bar{h}_1| + |\bar{h}_2|} \quad (4.14)$$

Here the reference length is $L_{ref} = h$, therefore $\bar{h}_1 + \bar{h}_2 = 1$ and $\varepsilon = |\bar{h}|_1$.

4.3 Steady State Two-liquid Electroosmotic Flow

4.3.1 Analytical solutions

For the steady state fully-developed flow, the dimensionless velocity for the aqueous solution, when Eq. (4.9a) is combined with Eq. (4.8), becomes

$$\frac{\partial^2 \bar{u}_1^E}{\partial \bar{z}^2} + \frac{\partial^2 \bar{u}_1^E}{\partial \bar{y}^2} = \text{Re} G_x \bar{\psi}(\bar{z}, \bar{y}) \quad (4.15a)$$

corresponding to the component driven by the electroosmotic forces and

$$\frac{\partial^2 \bar{u}_1^P}{\partial \bar{z}^2} + \frac{\partial^2 \bar{u}_1^P}{\partial \bar{y}^2} = \text{Re} \frac{d\bar{p}}{d\bar{x}} \quad (4.15b)$$

corresponding to the velocity component by the pressure gradient. Similarly, the velocity of the non-aqueous liquid is written in two components as

$$\frac{\partial^2 \bar{u}_2^E}{\partial \bar{z}^2} + \frac{\partial^2 \bar{u}_2^E}{\partial \bar{y}^2} = 0 \quad (4.15c)$$

corresponding to the velocity component influenced by the electroosmotic flow of the aqueous solution and

$$\frac{\partial^2 \bar{u}_2^P}{\partial \bar{z}^2} + \frac{\partial^2 \bar{u}_2^P}{\partial \bar{y}^2} = \frac{\text{Re}}{\beta} \frac{d\bar{p}}{d\bar{x}} \quad (4.15d)$$

corresponding to the velocity component by the pressure gradient.

Using the method of separation of variables and submitting the solution of $\bar{\psi}$ of

Eq. (4.3), the analytical velocity profile corresponding the electroosmotic forces, $\bar{u}_1^E$, is obtained as

$$\bar{u}_1^E(\bar{z}, \bar{y}) = \sum_{j=1}^{\infty} \left\{ \left[\sinh(\lambda_j \bar{y}) - \tanh(\lambda_j \bar{h}_1) \cosh(\lambda_j \bar{y}) \right] b1_j^E - \frac{\Phi_j(\bar{h}_1) \cosh(\lambda_j \bar{y})}{\cosh(\lambda_j \bar{h}_1)} + \Phi_j(\bar{y}) \right\} \cos(\lambda_j \bar{z}) \quad (4.16a)$$

from Eq. (4.15a). Other dimensionless velocity profiles of $\bar{u}_1^P$, $\bar{u}_2^E$ and $\bar{u}_2^P$ are also obtained, respectively

$$\begin{aligned} \bar{u}_1^P(\bar{z}, \bar{y}) = \sum_{j=1}^{\infty} \left\{ \frac{4\text{Re}(-1)^{j+1}}{(2j-1)\pi\lambda_j^2} \frac{d\bar{p}}{d\bar{x}} \left[\frac{\cosh(\lambda_j \bar{y})}{\cosh(\lambda_j \bar{h}_1)} - 1 \right] \right. \\ \left. + \left[\sinh(\lambda_j \bar{y}) - \tanh(\lambda_j \bar{h}_1) \cosh(\lambda_j \bar{y}) \right] b1_j^P \right\} \cos(\lambda_j \bar{z}) \end{aligned} \quad (4.16b)$$

$$\bar{u}_2^E(\bar{z}, \bar{y}) = \sum_{j=1}^{\infty} \left\{ \left[\sinh(\lambda_j \bar{y}) - \tanh(\lambda_j \bar{h}_2) \cosh(\lambda_j \bar{y}) \right] b2_j^E \right\} \cos(\lambda_j \bar{z}) \quad (4.16c)$$

$$\begin{aligned} \bar{u}_2^P(\bar{z}, \bar{y}) = \sum_{j=1}^{\infty} \left\{ \frac{4\text{Re}(-1)^{j+1}}{\beta(2j-1)\pi\lambda_j^2} \frac{d\bar{p}}{d\bar{x}} \left[\frac{\cosh(\lambda_j \bar{y})}{\cosh(\lambda_j \bar{h}_2)} - 1 \right] \right. \\ \left. + \left[\sinh(\lambda_j \bar{y}) - \tanh(\lambda_j \bar{h}_2) \cosh(\lambda_j \bar{y}) \right] b2_j^P \right\} \cos(\lambda_j \bar{z}) \end{aligned} \quad (4.16d)$$

where the parameter function, $\Phi_j(y)$, dependent on j and y , is defined by

$$\begin{aligned} \Phi_j(\bar{y}) = \frac{-4\text{Re}G_x \bar{\zeta}_1 (-1)^{j+1} \sinh(B_j \bar{y}) + 4\text{Re}G_x \bar{\zeta}_3 (-1)^{j+1} \sinh[B_j(\bar{h}_1 - \bar{y})]}{(2j-1)\pi(\lambda_j^2 - B_j^2) \sinh(B_j \bar{h}_1)} \\ - \sum_{p=1}^{\infty} \frac{4\text{Re}G_x \bar{\zeta}_2 [1 + (-1)^{p+1}] \lambda_j (-1)^{j+1} \sin(p\pi \bar{y}/\bar{h}_1)}{p\pi \bar{w}(\lambda_j^2 + A_p^2) [(p\pi/\bar{h}_1)^2 + \lambda_j^2]} \end{aligned} \quad (4.17)$$

The matching conditions, Eq. (4.11) can also be decomposed by

$$\begin{cases} \bar{u}_1^E(\bar{z}, 0) = \bar{u}_2^E(\bar{z}, 0) \\ \frac{\partial \bar{u}_1^E(\bar{z}, 0)}{\partial \bar{y}} = \beta \frac{\partial \bar{u}_2^E(\bar{z}, 0)}{\partial \bar{y}} - M \bar{\rho}_q^s(\bar{z}) \end{cases} \quad (4.18a)$$

and

$$\begin{cases} \bar{u}_1^P(\bar{z}, 0) = \bar{u}_2^P(\bar{z}, 0) \\ \frac{\partial \bar{u}_1^P(\bar{z}, 0)}{\partial \bar{y}} = \beta \frac{\partial \bar{u}_2^P(\bar{z}, 0)}{\partial \bar{y}} \end{cases} \quad (4.18b)$$

Substituting Eqs. (4.16a) and (4.16c) into Eq. (4.18a) and substituting Eqs. (4.16b) and (4.16d) into Eq. (4.18b), one can obtain the constants

$$b1_j^E = \beta b2_j^E + \frac{M}{\lambda_j} \rho_{qj}^s - \frac{\Phi_j'(0)}{\lambda_j} \quad (4.19a)$$

$$b2_j^E = \frac{\frac{M}{\lambda_j} \rho_{qj}^s \tanh(\lambda_j \bar{h}_1) + \frac{\Phi_j(\bar{h}_1)}{\cosh(\lambda_j \bar{h}_1)} - \frac{\Phi_j'(0)}{\lambda_j} \tanh(\lambda_j \bar{h}_1) - \Phi_j(0)}{\tanh(\lambda_j \bar{h}_2) - \beta \tanh(\lambda_j \bar{h}_1)} \quad (4.19b)$$

and

$$b1_j^P = \beta b2_j^P \quad (4.19c)$$

$$b2_j^P = \frac{\frac{4\text{Re}(-1)^{j+1}}{(2j-1)\pi\lambda_j^2} \frac{d\bar{p}}{d\bar{x}} \left[\frac{1}{\cosh(\lambda_j \bar{h}_1)} - 1 - \frac{1}{\cosh(\lambda_j \bar{h}_2)\beta} + \frac{1}{\beta} \right]}{\beta \tanh(\lambda_j \bar{h}_1) - \tanh(\lambda_j \bar{h}_2)} \quad (4.19d)$$

where the parameter function, Φ_j' is defined as

$$\begin{aligned} \Phi_j'(\bar{y}) = & \frac{-4\text{Re}G_x \bar{\zeta}_1(-1)^{j+1} B_j \cosh(B_j \bar{y}) + 4\text{Re}G_x \bar{\zeta}_3(-1)^{j+1} B_j \cosh[B_j(\bar{h}_1 - \bar{y})]}{(2j-1)\pi(\lambda_j^2 - B_j^2) \sinh(B_j \bar{h}_1)} \\ & - \sum_{p=1}^{\infty} \frac{4\text{Re}G_x \bar{\zeta}_2[1 + (-1)^{p+1}] \lambda_j (-1)^{j+1} \cos(p\pi \bar{y}/\bar{h}_1)}{\bar{w} \bar{h}_1 (\lambda_j^2 + A_p^2) [(p\pi/\bar{h}_1)^2 + \lambda_j^2]} \end{aligned} \quad (4.20)$$

and the contribution of surface charge, $\bar{\rho}_{qj}^s$, is the Fourier transform of $\bar{\rho}_q^s$

$$\begin{aligned} \bar{\rho}_{qj}^s = \frac{2}{\bar{w}} \int_0^{\bar{w}} \bar{\rho}_q^s(\bar{z}) \cos(\lambda_j \bar{z}) d\bar{z} = & -\frac{4\bar{\zeta}_3(-1)^{j+1}B_j}{(2j-1)\pi \tanh(B_j\bar{h}_1)} \\ & + \frac{4\bar{\zeta}_1(-1)^{j+1}B_j}{(2j-1)\pi \sinh(B_j\bar{h}_1)} - \sum_{p=1}^{\infty} \frac{4\bar{\zeta}_2[1+(-1)^{p+1}]\lambda_j(-1)^{j+1}}{\bar{h}_1\bar{w}(A_p^2 + \lambda_j^2)} \end{aligned} \quad (4.21)$$

The dimensionless volumetric flow rates through the rectangular channel can be defined by $\bar{q}_1 = \bar{q}_1^E + \bar{q}_1^P = q_1/(L_{\text{ref}}^2 U_{\text{ref}})$ and $\bar{q}_2 = \bar{q}_2^E + \bar{q}_2^P = q_2/(L_{\text{ref}}^2 U_{\text{ref}})$. The dimensionless flow rates are give by

$$\bar{q}_1^E = 2 \int_{\bar{h}_1}^0 \int_0^{\bar{w}} \bar{u}_1^E(\bar{z}, \bar{y}) d\bar{z} d\bar{y} \quad (4.22a)$$

$$\bar{q}_1^P = 2 \int_{\bar{h}_1}^0 \int_0^{\bar{w}} \bar{u}_1^P(\bar{z}, \bar{y}) d\bar{z} d\bar{y} \quad (4.22b)$$

and

$$\bar{q}_2^E = 2 \int_0^{\bar{h}_2} \int_0^{\bar{w}} \bar{u}_2^E(\bar{z}, \bar{y}) d\bar{z} d\bar{y} \quad (4.22c)$$

$$\bar{q}_2^P = 2 \int_0^{\bar{h}_2} \int_0^{\bar{w}} \bar{u}_2^P(\bar{z}, \bar{y}) d\bar{z} d\bar{y} \quad (4.22d)$$

Substituting $\bar{u}_1^E$, $\bar{u}_1^P$, $\bar{u}_2^E$ and $\bar{u}_2^P$ into Eq. (4.22), respectively, yields the dimensionless volumetric flow rates as

$$\bar{q}_1^E = 2 \sum_{j=1}^{\infty} \left\{ \left[1 - \frac{1}{\cosh(\lambda_j \bar{h}_1)} \right] \frac{b1_j^E}{\lambda_j} + \frac{\Phi_j(\bar{h}_1)}{\lambda_j} \tanh(\lambda_j \bar{h}_1) + \Phi_j^I(0) - \Phi_j^I(\bar{h}_1) \right\} \frac{\sin(\lambda_j \bar{w})}{\lambda_j} \quad (4.23a)$$

$$\bar{q}_1^P = 2 \sum_{j=1}^{\infty} \left\{ \left[1 - \frac{1}{\cosh(\lambda_j \bar{h}_1)} \right] \frac{b1_j^P}{\lambda_j} + \frac{4\text{Re}(-1)^{j+1} d\bar{p}}{(2j-1)\pi \lambda_j^2 d\bar{x}} \left(\frac{1}{\lambda_j} - \bar{h}_1 \right) \right\} \frac{\sin(\lambda_j \bar{w})}{\lambda_j} \quad (4.23b)$$

and

$$\bar{q}_2^E = 2 \sum_{j=1}^{\infty} \left[\frac{1}{\cosh(\lambda_j \bar{h}_2)} - 1 \right] \frac{b2_j^E}{\lambda_j} \sin(\lambda_j \bar{w}) \quad (4.23c)$$

$$\bar{q}_2^P = 2 \sum_{j=1}^{\infty} \left\{ \left[1 - \frac{1}{\cosh(\lambda_j \bar{h}_2)} \right] \frac{b2_j^P}{\lambda_j} + \frac{4\text{Re}(-1)^{j+1} d\bar{p}}{(2j-1)\pi \beta \lambda_j^2 d\bar{x}} \left(\frac{1}{\lambda_j} - \bar{h}_2 \right) \right\} \frac{\sin(\lambda_j \bar{w})}{\lambda_j} \quad (4.23d)$$

where the parameter function, Φ_j^I is defined as

$$\begin{aligned} \Phi_j^I(\bar{y}) = & \frac{-4\text{Re}G_x\bar{\zeta}_1(-1)^{j+1}\cosh(B_j\bar{y}) + 4\text{Re}G_x\bar{\zeta}_3(-1)^{j+1}\cosh[B_j(\bar{h}_1 - \bar{y})]}{(2j-1)\pi(\lambda_j^2 - B_j^2)\sinh(B_j\bar{h}_1)B_j} \\ & - \sum_{p=1}^{\infty} \frac{4\text{Re}G_x\bar{\zeta}_2[1 + (-1)^{p+1}]\lambda_j\bar{h}_1(-1)^{j+1}\cos(p\pi\bar{y}/\bar{h}_1)}{p^2\pi^2\bar{w}(\lambda_j^2 + A_p^2)[(p\pi/\bar{h}_1)^2 + \lambda_j^2]} \end{aligned} \quad (4.24)$$

4.3.2 Results of the steady state two-liquid EOF

The geometry used in this section is similar to section (4.1.2), the dimensions of the microchannel are 40 μm width and 40 μm height, respectively. The characteristic length L_{ref} is equal to the height of the channel. The concentration of the aqueous solution is chosen in the range from 10^{-6} to 10^{-5}M , and the electrical potential $E_x = 3\text{kV/m}$. The reference potential is adopted by $\zeta_{\text{ref}} = k_B T / (z_0 e) \approx 25.7\text{mV}$ at 25°C . Here we choose the wall zeta potentials as $\zeta_1 = \zeta_2 = -25\text{mV}$ as the default values. The viscosity and density of the KCL solution is $\mu_{\text{ref}} = 10^{-3}\text{Pa}\cdot\text{s}$ and $\rho_{\text{ref}} = 10^3\text{kg/m}^3$, respectively. With these reference potential and viscosity, the Helmholtz-Smoluchowski electroosmotic velocity is chosen as the reference velocity

$$U_{\text{ref}} = \frac{E_x \epsilon \zeta_{\text{ref}}}{\mu_{\text{ref}}} = 5.3 \times 10^{-5} \text{m/s} \quad (4.25)$$

It should be mentioned that these definitions, reference surface potential and reference velocity give $\text{Re}G = K^2$. This results in the same form of expression for Eq. (4.15a) and Eq. (4.1), the equation for potential are the same. The Reynolds number is

$$\text{Re} = \frac{\rho_{\text{ref}} U_{\text{ref}} L_{\text{ref}}}{\mu_{\text{ref}}} \approx 0.0021$$

Effect of the viscosity ratio, β

The flow characteristics depend on the coupling effect between the two liquids which involve the electrokinetic driving force in the aqueous solution and the interfacial phe-

Figure 4.3: Dimensionless velocity distributions at the symmetric line for different viscosity ratios.

nomenon. The interfacial phenomenon is obtained from the balance of the modified stress force $P + T^M$ as shown in Eq. (3.26), which involves the opposite electrostatic force exerted on the interface and the hydrodynamic shear stress between the two liquids. Here it is represented by the matching conditions as Eq. (4.10b). The velocity at the liquid-liquid interface must match, i.e. the aqueous solution and the non-aqueous velocities must be the same and the forces must be balanced at the interface. The coupled two fluids velocities are presented by Eq. (4.11). To investigate the effect of viscosity ratio between the two fluids, the values are chosen as $\beta = 1, 10$ and 100 . Fig. 4.3 shows the dimensionless velocity profiles at the symmetric line when $\beta = 1, 10$ and 100 and the surface zeta potential is half of the zeta potential at the bottom wall $\zeta_3 = \zeta_1$.

The electrical body force is resulted from the interaction of the electric field and the net charge density. This driving force exists only within the non-neutral charges region - the electrical double layer in the aqueous solution. Liquid outside the EDL regions is set in motion passively due to the hydrodynamic shear stress. The velocity profile of the non-aqueous fluid is also passive, very much like the Couette flow. It is purely due to the interfacial shear stress dragged by the aqueous solution on the non-aqueous liquid.

The results indicate that the velocity profiles of the high EO mobility are dependent on the viscosity ratio, β . While the viscosity ratio is small, the flow resistance of the non-aqueous liquid is small, the non-aqueous liquid can be driven with less flow resistance as shown in Fig. 4.3. When the viscosity ratio is higher, the flow resistance of the non-aqueous liquid is higher, resulting in a steeper velocity gradient at the interface of the aqueous solution as shown in Fig. 4.3.

Figure 4.4: Comparison of the analytical solution between the two-fluid model and the single-fluid model. The viscosity ratio between the two liquids is $\beta = 10^4$.

For an extreme case, the infinite viscosity of the non-aqueous liquid makes the flow of the non-aqueous liquid resembles to that of the channel wall. Hence the flow of the aqueous solution resembles to the single-fluid EOF, through which we can compare the results of the steady state analytical model with those of the previous works. If the channel width is much larger than the channel height, in the fully-developed state, the flow profile at the symmetric section in this channel is identical with the flow between two infinite parallel flat plates. For two infinite parallel flat plates, if the zeta potentials are assumed as the same at two plates, Patankar and Hu [1998] presented an analytical result of the streamwise velocity,

$$\bar{u}(\bar{y}) = \zeta_1 \left[\frac{\cosh(K\bar{t} - K\bar{h}_1/2)}{\cosh(K\bar{h}_1/2)} - 1 \right] \quad (4.26)$$

Figure 4.4 shows the comparison between the present exact velocity profile of the high EO mobility fluid from the two-fluid model when $\beta = 10^4$, and the exact solution from Eq. (4.26). In this figure, the channel is chosen as $60 \mu\text{m}$ width and $20 \mu\text{m}$ height. It is clearly seen that the two results from different models are identical.

Effect of the interfacial zeta potential

Figure 4.5: Dimensionless velocity distributions at the symmetric line for different interfacial zeta potential.

The fluid-fluid interfacial zeta potential depends on the properties of two fluids. it varies with the pH value, the concentration of the liquid and the ionic surfactants [Gu and Li, 1997]. The surface free charge density at the interface is directly related to the interface zeta potential, ζ_3 , as shown by Eq. (4.6). The free charges at the interface influence the local net charge distribution in the region close to the interface (which is the electrical double layer), hence the electroosmotic driving force within the EDL regions. On other hand, the interaction between this surface free charge density and the externally applied electric field generates a force at the interface as shown by Eq.

(4.10b). Because of the opposite sign, this surface force at the interface act in the opposite direction to the electroosmotic body force in the EDL. To analyze the effects of the interface zeta potential, ζ_3 is assigned as ζ_1 , $0.5\zeta_1$ and zero, respectively. Fig. 4.5 shows the velocity profile at the symmetric line for different interfacial zeta potential when the viscosity ratio, $\beta = 1$. It is shown that the velocity profiles of two liquids are strongly dependent on the interfacial zeta potential, ζ_3 . A lower interface zeta potential would result in a higher velocity of the non-aqueous liquid. This is because that with a high interfacial zeta potential, the interface experiences a higher opposite force. If the interfacial zeta potential equals the wall zeta potential, the velocity of the non-aqueous liquid approaches zero, as the driving force within EDLs is not strong to drive the non-aqueous liquid to flow.

Effect of the EDL parameter, K

Figure 4.6: Dimensionless velocity distributions at the symmetric line for different values of K when $\beta = 1$ and $\zeta_3 = 0.5\zeta_1$.

Figure 4.6 shows the non-dimensional velocity profiles for different values of K when $\beta = 1$ and $\zeta_3 = 0.5\zeta_1$. The Debye length, $1/\kappa$, is referred to the characteristic thickness of the EDL. It can be seen that $1/\kappa$ decreases inversely as the square root of the

concentration. But the increasing of the electroosmotic force is proportional to the bulk ionic concentration. As the result, though the EDL is thinner when the concentration is 10^{-5}M ($K = 412$), the overall velocities are a little larger than those when the concentration is 10^{-7}M ($K = 41.2$). The smaller value of K means a thicker EDL. From Fig. 4.6, it is noted that the affecting region is thicker when $K = 41.2$ than $K = 130$.

Effect of the aspect ratio, χ

Figure 4.7: Dimensionless velocity distributions at the symmetric line for different aspect ratio of pure electroosmotic flow.

The effect of the aspect ratio, $\chi = h/(2w)$, is shown in Fig. 4.7, where $\beta = 1$ and $\zeta_3 = 0.5\zeta_1$. Here the varieties of χ are achieved by changing the w at constant $h = 40\mu\text{m}$. The higher value of χ means a thinner channel where the effect of two side walls is more significant. In such situation, the cross section cannot be simplified to 1D model. The aspect ratios are large for most microchannels. This is the reason why a 2D model is developed in this work.

This point is clearer from the results of pure pressure gradient flow as shown in Fig. 4.8. At small aspect ratio, it is well known that the velocity represents as parabolic shape for a single-fluid or two-fluid with same viscosity. At large aspect ratio, where the

Figure 4.8: Dimensionless velocity distributions at the symmetric line for different aspect ratio of pure pressure driven flow. For $chi = 1$, the dimensionless pressure gradient is $d\bar{p}/d\bar{x} = 300$, for $\chi = 5$, $d\bar{p}/d\bar{x} = 3000$ and for $\chi = 10$, $d\bar{p}/d\bar{x} = 10^4$

effect of side wall becomes significant, however, the flow presents 'plug' shape as shown in Fig. 4.8.

4.4 Transient Two-liquid Electroosmotic Flow

4.4.1 Analytical solutions

Substituting the local volumetric net charge density, Eq. (4.3), into Eq. (4.9a) yields the transient momentum equation for the aqueous solution

$$\text{Re} \frac{\partial \bar{u}_1^E(\bar{z}, \bar{y}, \bar{t})}{\partial \bar{t}} = \frac{\partial^2 \bar{u}_1^E(\bar{z}, \bar{y}, \bar{t})}{\partial \bar{z}^2} + \frac{\partial^2 \bar{u}_1^E(\bar{z}, \bar{y}, \bar{t})}{\partial \bar{y}^2} - \text{Re} G_x \bar{\psi}(\bar{z}, \bar{y}) \quad (4.27a)$$

for the velocity component driven by the electroosmotic force and

$$\text{Re} \frac{\partial \bar{u}_1^P(\bar{z}, \bar{y}, \bar{t})}{\partial \bar{t}} = \frac{\partial^2 \bar{u}_1^P(\bar{z}, \bar{y}, \bar{t})}{\partial \bar{z}^2} + \frac{\partial^2 \bar{u}_1^P(\bar{z}, \bar{y}, \bar{t})}{\partial \bar{y}^2} - \text{Re} \frac{d\bar{p}}{d\bar{x}} \quad (4.27b)$$

for the component by pressure gradient. Similarly, the two components of the non-aqueous liquid are

$$\frac{\text{Re}}{\alpha} \frac{\partial \bar{u}_2^E(\bar{z}, \bar{y}, \bar{t})}{\partial \bar{t}} = \frac{\partial^2 \bar{u}_2^E(\bar{z}, \bar{y}, \bar{t})}{\partial \bar{z}^2} + \frac{\partial^2 \bar{u}_2^E(\bar{z}, \bar{y}, \bar{t})}{\partial \bar{y}^2} \quad (4.27c)$$

for the component influenced by the aqueous solution and

$$\frac{\text{Re}}{\alpha} \frac{\partial \bar{u}_2^P(\bar{z}, \bar{y}, \bar{t})}{\partial \bar{t}} = \frac{\partial^2 \bar{u}_2^P(\bar{z}, \bar{y}, \bar{t})}{\partial \bar{z}^2} + \frac{\partial^2 \bar{u}_2^P(\bar{z}, \bar{y}, \bar{t})}{\partial \bar{y}^2} - \frac{\text{Re}}{\beta} \frac{d\bar{p}}{d\bar{x}} \quad (4.27d)$$

for the component by pressure gradient. Here α is the kinematic viscosity ratio, defined as $\alpha = \nu_2/\nu_1$.

The Laplace transform method is applied to solve these equations. The Laplace transform of Eq. (4.27a) and Eq. (4.27b) is

$$\frac{\partial^2 \bar{U}_1^E(\bar{z}, \bar{y}, s)}{\partial \bar{z}^2} + \frac{\partial^2 \bar{U}_1^E(\bar{z}, \bar{y}, s)}{\partial \bar{y}^2} = s\text{Re}\bar{U}_1^E(\bar{z}, \bar{y}, s) + \frac{\text{Re}G_x\bar{\rho}_q(\bar{z}, \bar{y})}{s} \quad (4.28a)$$

and

$$\frac{\partial^2 \bar{U}_1^P(\bar{z}, \bar{y}, s)}{\partial \bar{z}^2} + \frac{\partial^2 \bar{U}_1^P(\bar{z}, \bar{y}, s)}{\partial \bar{y}^2} = s\text{Re}\bar{U}_1^P(\bar{z}, \bar{y}, s) + \frac{\text{Re}(d\bar{p}/d\bar{x})}{s} \quad (4.28b)$$

where s is the Laplace transform parameter. Similarly, the Laplace transforms of Eqs. (4.27c) and (4.27d) are

$$\frac{\partial^2 \bar{U}_2^E(\bar{z}, \bar{y}, s)}{\partial \bar{z}^2} + \frac{\partial^2 \bar{U}_2^E(\bar{z}, \bar{y}, s)}{\partial \bar{y}^2} = \frac{s\text{Re}}{\alpha} \bar{U}_2^E(\bar{z}, \bar{y}, s) \quad (4.28c)$$

and

$$\frac{\partial^2 \bar{U}_2^P(\bar{z}, \bar{y}, s)}{\partial \bar{z}^2} + \frac{\partial^2 \bar{U}_2^P(\bar{z}, \bar{y}, s)}{\partial \bar{y}^2} = \frac{s\text{Re}}{\alpha} \bar{U}_2^P(\bar{z}, \bar{y}, s) + \frac{\text{Re}(d\bar{p}/d\bar{x})}{\beta s} \quad (4.28d)$$

The Laplace transform of the boundary conditions are

$$\left\{ \begin{array}{l} \partial \bar{U}_1^E(0, \bar{y}, s) / \partial \bar{z} = 0 \\ \bar{U}_1^E(\bar{w}, \bar{y}, s) = 0 \\ \bar{U}_1^E(\bar{z}, \bar{h}_1, s) = 0 \end{array} \right. \quad \text{and} \quad \left\{ \begin{array}{l} \partial \bar{U}_1^P(0, \bar{y}, s) / \partial \bar{z} = 0 \\ \bar{U}_1^P(\bar{w}, \bar{y}, s) = 0 \\ \bar{U}_1^P(\bar{z}, \bar{h}_1, s) = 0 \end{array} \right. \quad (4.29a)$$

and

$$\left\{ \begin{array}{l} \partial \bar{U}_2^E(0, \bar{y}, s) / \partial \bar{z} = 0 \\ \bar{U}_2^E(\bar{w}, \bar{y}, s) = 0 \\ \bar{U}_2^E(\bar{z}, \bar{h}_1, s) = 0 \end{array} \right. \quad \text{and} \quad \left\{ \begin{array}{l} \partial \bar{U}_2^P(0, \bar{y}, s) / \partial \bar{z} = 0 \\ \bar{U}_2^P(\bar{w}, \bar{y}, s) = 0 \\ \bar{U}_2^P(\bar{z}, \bar{h}_1, s) = 0 \end{array} \right. \quad (4.29b)$$

The Laplace transform of the matching conditions at the liquid-liquid interface are

$$\left\{ \begin{array}{l} \bar{U}_1^E(\bar{z}, 0, s) = \bar{U}_2^E(\bar{z}, 0, s) \\ \frac{\partial \bar{U}_1^E(\bar{z}, 0, s)}{\partial \bar{y}} = \beta \frac{\partial \bar{U}_2^E(\bar{z}, 0, s)}{\partial \bar{y}} - \frac{M \bar{\rho}_q^s}{s} \end{array} \right. \quad \text{and} \quad \left\{ \begin{array}{l} \bar{U}_1^P(\bar{z}, 0, s) = \bar{U}_2^P(\bar{z}, 0, s) \\ \frac{\partial \bar{U}_1^P(\bar{z}, 0, s)}{\partial \bar{y}} = \beta \frac{\partial \bar{U}_2^P(\bar{z}, 0, s)}{\partial \bar{y}} \end{array} \right. \quad (4.30)$$

By the separation of variables method, the solutions of Eqs. (4.28a) and (4.28b) with the boundary conditions, Eq. (4.29a), give

$$\bar{U}_1^E(\bar{z}, \bar{y}, s) = \sum_{j=1}^{\infty} \left\{ \left[\sinh(D_j \bar{y}) - \tanh(D_j \bar{h}_1) \cosh(D_j \bar{y}) \right] b1_j^E(s) - \frac{\Phi_j(\bar{h}_1, s) \cosh(D_j \bar{y})}{\cosh(D_j \bar{h}_1)} + \Phi_j(\bar{y}, s) \right\} \cos(\lambda_j \bar{z}) \quad (4.31a)$$

$$\bar{U}_1^P(\bar{z}, \bar{y}, s) = \sum_{j=1}^{\infty} \left\{ \frac{4 \operatorname{Re}(-1)^{j+1}}{(2j-1)s\pi D_j^2} \frac{d\bar{p}}{d\bar{x}} \left[\frac{\cosh(D_j \bar{y})}{\cosh(D_j \bar{h}_1)} - 1 \right] + \left[\sinh(D_j \bar{y}) - \tanh(D_j \bar{h}_1) \cosh(D_j \bar{y}) \right] b1_j^P(s) \right\} \cos(\lambda_j \bar{z}) \quad (4.31b)$$

And the solution of Eqs. (4.28c) and (4.28d) with the boundary conditions Eq. (4.29b)

are

$$\bar{U}_2^E(\bar{z}, \bar{y}, s) = \sum_{j=1}^{\infty} [\sinh(E_j \bar{y}) - \tanh(E_j \bar{h}_2) \cosh(E_j \bar{y})] b2_j^E(s) \cos(\lambda_j \bar{z}) \quad (4.31c)$$

$$\begin{aligned} \bar{U}_2^P(\bar{z}, \bar{y}, s) = \sum_{j=1}^{\infty} \left\{ \frac{4\text{Re}(-1)^{j+1}}{(2j-1)s\pi\beta E_j^2} \frac{d\bar{p}}{d\bar{x}} \left[\frac{\cosh(E_j \bar{y})}{\cosh(E_j \bar{h}_2)} - 1 \right] \right. \\ \left. + [\sinh(E_j \bar{y}) - \tanh(E_j \bar{h}_2) \cosh(E_j \bar{y})] b2_j^P(s) \right\} \cos(\lambda_j \bar{z}) \end{aligned} \quad (4.31d)$$

Here

$$\begin{cases} D_j = \sqrt{\lambda^2 + s\text{Re}} \\ E_j = \sqrt{\lambda^2 + s\text{Re}/\alpha} \end{cases} \quad (4.32)$$

With the matching conditions (4.30), the coefficient $b1_j^E(s)$, $b1_j^P(s)$, $b2_j^E(s)$ and $b2_j^P(s)$ can be obtained as

$$b1_j^E(s) = \beta \frac{E_j}{D_j} b2_j^E(s) - \frac{M}{D_j s} \bar{\rho}_{qj}^s - \frac{\Phi'(0, s)}{D_j} \quad (4.33a)$$

$$b1_j^P(s) = \beta \frac{E_j}{D_j} b2_j^P(s) \quad (4.33b)$$

$$b2_j^E(s) = \frac{\frac{\Phi_j(\bar{h}_1, s)}{\cosh(D_j \bar{h}_1)} - \left(\frac{M \bar{\rho}_{qj}^s}{s} + \Phi_j'(0, s) \right) \frac{\tanh(D_j \bar{h}_1)}{D_j} - \Phi_j(0, s)}{\tanh(E_j \bar{h}_2) - \beta \frac{E_j}{D_j} \tanh(D_j \bar{h}_1)} \quad (4.33c)$$

$$b2_j^P(s) = \left[\frac{4\text{Re}(-1)^{j+1}}{(2j-1)s\pi} \frac{d\bar{p}}{d\bar{x}} \right] \frac{\frac{1}{\beta E_j^2} \left[\frac{1}{\cosh(E_j \bar{h}_2)} - 1 \right] - \frac{1}{D_j^2} \left[\frac{1}{\cosh(D_j \bar{h}_1)} - 1 \right]}{\tanh(E_j \bar{h}_2) - \beta \frac{E_j}{D_j} \tanh(D_j \bar{h}_1)} \quad (4.33d)$$

Here the parameter function $\Phi_j(\bar{y}, s)$ is different from the $\Phi_j(\bar{y})$ of Eq. (4.17) and is

defined as

$$\begin{aligned} \Phi_j(\bar{y}, s) = & \frac{-4\text{Re}G_x\bar{\zeta}_1(-1)^{j+1}\sinh(B_j\bar{y}) + 4\text{Re}G_x\bar{\zeta}_3(-1)^{j+1}\sinh[B_j(\bar{h}_1 - \bar{y})]}{(2j-1)\pi(\lambda_j^2 + s - B_j^2)\sinh(B_j\bar{h}_1)s} \\ & - \sum_{p=1}^{\infty} \frac{4\text{Re}G_x\bar{\zeta}_2[1 + (-1)^{p+1}]\lambda_j(-1)^{j+1}\sin(p\pi\bar{y}/\bar{h}_1)}{p\pi\bar{w}s(\lambda_j^2 + A_p^2)[(p\pi/\bar{h}_1)^2 + s + \lambda_j^2]} \end{aligned} \quad (4.34)$$

Similarly, the parameter function $\Phi'_j(\bar{y}, s)$ is defined as

$$\begin{aligned} \Phi'_j(\bar{y}, s) = & \frac{-4\text{Re}G_x\bar{\zeta}_1(-1)^{j+1}B_j\cosh(B_j\bar{y}) + 4\text{Re}G_x\bar{\zeta}_3(-1)^{j+1}B_j\cosh[B_j(\bar{h}_1 - \bar{y})]}{(2j-1)\pi(\lambda_j^2 + s - B_j^2)\sinh(B_j\bar{h}_1)s} \\ & - \sum_{p=1}^{\infty} \frac{4\text{Re}G_x\bar{\zeta}_2[1 + (-1)^{p+1}]\lambda_j(-1)^{j+1}\cos(p\pi\bar{y}/\bar{h}_1)}{\bar{w}\bar{h}_1(\lambda_j^2 + A_p^2)[(p\pi/\bar{h}_1)^2 + s + \lambda_j^2]s} \end{aligned} \quad (4.35)$$

This is different from the definition of $\Phi'_j(\bar{y})$ in Eq. (4.20).

The transient volumetric flow rates for two liquids are defined as

$$\bar{q}_1^E(\bar{t}) = 2 \int_{\bar{h}_1}^0 \int_0^{\bar{w}} \bar{u}_1^E(\bar{z}, \bar{y}, \bar{t}) d\bar{x} d\bar{y} \quad (4.36a)$$

$$\bar{q}_1^P(\bar{t}) = 2 \int_{\bar{h}_1}^0 \int_0^{\bar{w}} \bar{u}_1^P(\bar{z}, \bar{y}, \bar{t}) d\bar{x} d\bar{y} \quad (4.36b)$$

$$\bar{q}_2^E(\bar{t}) = 2 \int_0^{\bar{h}_2} \int_0^{\bar{w}} \bar{u}_2^E(\bar{z}, \bar{y}, \bar{t}) d\bar{x} d\bar{y} \quad (4.36c)$$

and

$$\bar{q}_2^P(\bar{t}) = 2 \int_0^{\bar{h}_2} \int_0^{\bar{w}} \bar{u}_2^P(\bar{z}, \bar{y}, \bar{t}) d\bar{x} d\bar{y} \quad (4.36d)$$

The Laplace transform of above equations are

$$\bar{Q}_1^E(s) = 2 \int_{\bar{h}_1}^0 \int_0^{\bar{w}} \bar{U}_1^E(\bar{z}, \bar{y}, s) d\bar{x} d\bar{y} \quad (4.37a)$$

$$\bar{Q}_1^P(s) = 2 \int_{\bar{h}_1}^0 \int_0^{\bar{w}} \bar{U}_1^P(\bar{z}, \bar{y}, s) d\bar{x} d\bar{y} \quad (4.37b)$$

$$\bar{Q}_2^E(s) = 2 \int_0^{\bar{h}_2} \int_0^{\bar{w}} \bar{U}_2^E(\bar{z}, \bar{y}, s) d\bar{x} d\bar{y} \quad (4.37c)$$

and

$$\bar{Q}_2^P(s) = 2 \int_0^{\bar{h}_2} \int_0^{\bar{w}} \bar{U}_2^P(\bar{z}, \bar{y}, s) d\bar{x} d\bar{y} \quad (4.37d)$$

Substituting the solution of $\bar{Q}_1^E$, $\bar{Q}_1^P$, $\bar{Q}_2^E$ and $\bar{Q}_2^P$, the dimensionless volumetric flow rates are obtained as

$$\begin{aligned} \bar{Q}_1^E(s) = 2 \sum_{j=1}^{\infty} \left\{ \left[1 - \frac{1}{\cosh(D_j \bar{h}_1)} \right] \frac{b1_j^E(s)}{D_j} + \frac{\Phi_j(\bar{h}_1, s) \sinh(D_j \bar{h}_1)}{\cosh(D_j \bar{h}_1) D_j} \right. \\ \left. + I_j^\Phi(0, s) - I_j^\Phi(\bar{h}_1, s) \right\} \frac{\sin(\lambda_j \bar{w})}{\lambda_j} \end{aligned} \quad (4.38a)$$

$$\bar{Q}_1^P(s) = 2 \sum_{j=1}^{\infty} \left\{ \left[1 - \frac{1}{\cosh(D_j \bar{h}_1)} \right] \frac{b1_j^P(s)}{D_j} + \frac{4\text{Re}(-1)^{j+1}}{(2j-1)\pi s D_j^2} \frac{d\bar{p}}{d\bar{x}} \left(\frac{1}{D_j} - \bar{h}_1 \right) \right\} \frac{\sin(\lambda_j \bar{w})}{\lambda_j} \quad (4.38b)$$

$$\bar{Q}_2^E(s) = 2 \sum_{j=1}^{\infty} \left[1 - \frac{1}{\cosh(E_j \bar{h}_2)} \right] \frac{b2_j^E(s)}{\lambda_j E_j} \sin(\lambda_j \bar{w}) \quad (4.38c)$$

$$\bar{Q}_2^P(s) = 2 \sum_{j=1}^{\infty} \left\{ \left[1 - \frac{1}{\cosh(E_j \bar{h}_2)} \right] \frac{b2_j^P(s)}{E_j} + \frac{4\text{Re}(-1)^{j+1}}{(2j-1)\pi s \beta E_j^2} \frac{d\bar{p}}{d\bar{x}} \left(\frac{1}{E_j} - \bar{h}_2 \right) \right\} \frac{\sin(\lambda_j \bar{w})}{\lambda_j} \quad (4.38d)$$

where

$$\begin{aligned} \Phi_j^I(\bar{y}, s) = \frac{-4\text{Re}G_x \bar{\zeta}_1 (-1)^{j+1} \cosh(B_j \bar{y}) + 4\text{Re}G_x \bar{\zeta}_3 (-1)^{j+1} \cosh[B_j(\bar{h}_1 - \bar{y})]}{(2j-1)\pi(\lambda_j^2 + s - B_j^2) \sinh(B_j \bar{h}_1) s B_j} \\ - \sum_{p=1}^{\infty} \frac{4\text{Re}G_x \bar{\zeta}_2 [1 + (-1)^{p+1}] \lambda_j \bar{h}_1 (-1)^{j+1} \cos(p\pi \bar{y}/\bar{h}_1)}{p^2 \pi^2 \bar{w} (\lambda_j^2 + A_p^2) [(p\pi/\bar{h}_1)^2 + s + \lambda_j^2] s} \end{aligned} \quad (4.39)$$

To obtain the final results, it is required to applied inversions of Laplace transform on velocities $\bar{U}_1^E$, $\bar{U}_1^P$, $\bar{U}_2^E$ and $\bar{U}_2^P$, and flow rates $\bar{Q}_1^E$, $\bar{Q}_1^P$, $\bar{Q}_2^E$ and $\bar{Q}_2^P$. Due to the complex nature of those forms, the numerical inversion of Laplace transforms method

— Gaver-Stehfest method with double precision [Maillet et al., 2000, chp. 9], is applied. The detail is shown in Appendix B.

4.4.2 Results of the transient two-liquid EOF

In this analysis, the geometry and other conditions are described in sub-section 4.3.2. The reference length is $L_{\text{ref}} = 40\mu\text{m}$ and the reference velocity is $U_{\text{ref}} = 5.3 \times 10^{-5}\text{m/s}$. Therefore, one obtains $t_{\text{ref}} \approx 0.755\text{s}$.

The two-liquid flow is driven by the electric body force resulted from the interaction of the external electric field with the volumetric local net charges in the aqueous solution, Eq. (4.8), and electric surface force from the interaction of the external electric field on the interface free charges, Eq. (4.6). Because of opposite sign, the surface charges at the interface generate a force at the interface and this force acts in the opposite direction to the electroosmotic body force in the EDL region at the vicinity of the interface. Fig. 4.9 shows the 3-D time evolution of the velocity profiles for the two-liquid electroosmotic flow due to the combined effects of the driving forces within the EDL regions of the aqueous solution and the force exerted on the interface. The kinematic viscosity ratio $\alpha = 1.5$ and the dynamic viscosity ratio $\beta = 1$. The interface zeta potential, ζ_3 is chosen as half of the zeta potential ($\zeta_3 = 0.5\zeta_1$) of the bottom wall and the zeta potentials of the two walls are assumed to be the same ($\zeta_2 = \zeta_1$). From the results shown in Fig. 4.9, it can be seen that upon the application of the electric field, the flow is activated in regions close to the channel walls and the interface. The velocity of the aqueous solution increases from zero in the same direction within the EDL regions close to the walls and the interface. But the effects of the force from the free charges of the interface cause the interface velocity to increase rapidly in the opposite direction. This is because the interface charges are equal to the total net charges within the EDL regions, close to the interface. The velocity at the interface region is significantly influenced by the surface force during the initial transient state. As time elapses, the liquid inside the EDLs exerts

a hydrodynamic shear stress on its adjacent liquid; the liquid outside the EDL regions may be considered as 'passive' flow caused by shear viscous forces.

The surface free charge density at the interface is directly related to the interface zeta potential, ζ_3 , by Eq. (4.6). The free charges at the interface influences the local net charge distribution in the region close to the interface, hence the driving force within the EDL regions. On other hand, the interaction between this surface free charge density and the externally applied electric field generates a force exerted on the interface as shown by matching condition Eq. (4.10b). Because of the opposite sign, this surface force at interface acts in the opposite direction of those in bulk. To analyze the effects of the interface zeta potential, ζ_3 is chosen as ζ_1 , $0.5\zeta_1$ and zero, respectively. Figs. 4.10 and 4.11 show the time evolution of the velocity profile when the dynamic viscosity ratio $\beta = 1$ and 10, respectively. Figs. 4.10(a) and 4.11(a) show that with a high interface zeta potential, the interface experiences a higher opposite force. At steady state, the velocity of the non-aqueous liquid approaches zero, as the driving force within the EDLs is not strong enough to drive the non-aqueous liquid.

It can be seen that during the initial transient time, the non-aqueous liquid moves in the opposite direction. As time elapses, negative velocity reduces as the EDLs exert a hydrodynamic shear stress on its adjacent liquid. The flow characteristics depend on the coupling effects between the two liquids, which involve the electrokinetic driving force in the aqueous solution and the interface phenomenon. The interface phenomenon includes the opposite force exerted on the interface and the interfacial shear stress between the two liquids.

Figures 4.10(c) and 4.11(c) show the time evolution in the absence of the zeta potential at the liquid-liquid interface. The velocity profile is completely different in the absence of the surface charge. Upon the application of the electric field, the flow is activated in the EDL regions near the channel walls in the aqueous solution. As there is no opposite force exerted on the interface, the non-aqueous liquid is delivered by electroosmosis of the aqueous solution, through the hydrodynamic viscous forces at the interface.

Figure 4.9: Developing process for two-liquid electroosmotic flow ($K = 130$, $\alpha = 1.5$, $\beta = 1$ and $\zeta_1 = \zeta_2 = 0.5\zeta_3$), (continued).

Figure 4.9: Developing process for two-liquid electroosmotic flow ($K = 130$, $\alpha = 1.5$, $\beta = 1$ and $\zeta_1 = \zeta_2 = 0.5\zeta_3$).

(a) $\zeta_3 = \zeta_1$

Figure 4.10: Dimensionless transient two-liquid velocities at the symmetric line for different zeta potentials ($K = 130$, $\alpha = 1.5$ and $\beta = 1$), (continued).

From these figures, it is noted that a lower interface zeta potential would result in a higher velocity of the non-aqueous liquid.

The results further indicate that the velocity profiles of the two-liquid flow are dependent on the viscosity ratio, β . When the viscosity ratio is high, the flow resistance of the 'passive' non-aqueous liquid is high, resulting in a steeper velocity gradient at the interface, as shown in Fig. 4.11. When the viscosity ratio is small, the non-aqueous liquid is relatively easy to be dragged by the same aqueous solution. It is observed that the negative velocity at the interface increases with a reduction in the viscosity ratio.

Figure 4.12 shows the effects of parameter K on the two-liquid flow when $K = 41$ and $K = 410$, respectively. As shown in Fig. 4.12, when the value of K is small, the EDL is thicker and extends into the bulk electrolyte. In 4.12(a), it is obvious that the activated regions are thicker than those in 4.12(b). This influences the distribution of two-liquid flow significantly. It is shown that a higher value of K (a lower concentration of the aqueous solution or a larger size of the channel) induces a larger velocity. This is because at the same channel geometry, a higher value of K corresponds to a higher

(b) $\zeta_3 = 0.5\zeta_1$

(c) $\zeta_3 = 0$

Figure 4.10: Dimensionless transient two-liquid velocities at the symmetric line for different zeta potentials ($K = 130$, $\alpha = 1.5$ and $\beta = 1$).

(a) $\zeta_3 = \zeta_1$

Figure 4.11: Dimensionless transient two-liquid velocities at the symmetric line for different zeta potentials ($K = 130$, $\alpha = 1.5$ and $\beta = 10$), (continued).

concentration. This results in a larger electroosmotic forces, though with a thinner EDL region.

Comparisons with the steady state solution are shown in Figs. 4.10 to 4.12 for different interface zeta potentials, viscosity ratios and concentrations. When the two-liquid flow approaches fully developed state (steady state), the flow velocities calculated by the numerical inversion of Laplace transform method agree well with the solutions obtained for steady state cases.

(b) $\zeta_3 = 0.5\zeta_1$

(c) $\zeta_3 = 0$

Figure 4.11: Dimensionless transient two-liquid velocities at the symmetric line for different zeta potentials ($K = 130$, $\alpha = 1.5$ and $\beta = 10$).

(a) $K = 41$

(b) $K = 410$

Figure 4.12: Dimensionless transient two-liquid velocities at the symmetric line for different value of K ($\alpha = 1.5$, $\beta = 10$ and $\zeta_3 = 0.5\zeta_1$).

4.5 Electroosmotic Control of the Interface between Two-liquid Flow

In most situations, the interface between two fluids is required to be controlled precisely [Kamholz et al., 2004; Weigl et al., 2001]. In the H-filter and T-sensor, fixed location of the interface at the exit facilitates the separation of the two fluids. In the flow switching devices [Blankenstein et al., 1996], the controlled interface can be manipulated and guide the sample flow into different outlet ports.

Recent works have employed hydrodynamic forces to control the interface between two fluids. By adjusting the volumetric flow rates of the input streams, Stiles and Fletcher [2004] have showed that the hydrodynamic widening and narrowing can be controlled. They presented a model to estimate the interface location in a horizontal microchannel. Lee et al. [2001a,b] presented a pre-focused multi-sample switch. The sample stream is constrained by two neighboring sheath flow. By controlling the sheath flow rates, the sample flow is guided into the desired outlet port without smearing into other ports. However, the proposed designs require high flow rate ratio to move the interface location or switch the sample fluid. Those call for micropump and increase design and cost issues.

More recently, electroosmotic force was introduced to achieve the confinement. Lin et al. [2002] proposed a numerical simulation of electrokinetic control model, which allows the volume of the sample to be controlled. Fu et al. [2004] presented experimental and numerical investigations into electrokinetic flow injection. By applying different voltage, the sample was directed into the specified outlet channel.

In this work, a novel concept to control the interface position using electroosmosis is presented. A H-shaped microfluidic device is used to demonstrate the concept in Fig. 4.13. Two fluids, (an aqueous solution, e.g. NaCl and a non-aqueous liquid, e.g. Glycerol) are introduced through the inlets by a syringe pump. To illustrate the concept, the volumetric flow rate of the two fluids are maintained to be the same. Electric

Figure 4.13: Schematic representation of the H-shaped microchannel

field is applied on the aqueous solution side. Thus electroosmotic effect results for the aqueous liquid side. When a positive electric field is applied between A and B (A as the positive electrode, B as the negative electrode), the electroosmotic force will drag the aqueous solution to facilitate its flow in the same direction as the pressure-driven flow. The average velocity of the aqueous liquid becomes faster. Thus the aqueous liquid will occupy a smaller channel width to maintain the fixed flowrate, and the interface position will be shifted away from the center position as depicted in Fig. 4.14(b). When a negative electric field is applied across A and B, an opposite electroosmotic flow will be resulted which is against the pressure driven flow. More resistance force will be encountered to drive the aqueous liquid. The aqueous liquid is flowing at a small velocity due to the electroosmotic effect, thus occupies a larger channel width and the interface position will be shifted to center line as depicted in Fig. 4.14(c). Hence, by adjusting the direction and strength of the applied electric field, the interface position can be controlled.

4.5.1 Interface Position

In the previous section 4.3, analytical solutions of two-liquid flow driven by electroosmosis and pressure gradient are obtained. To demonstrate the flow characteristics, the

Figure 4.14: Schematic of interface control using electroosmotic effect.

velocities and flow rates are calculated for a given set of externally applied electric field, pressure gradient and hold up, ε). This section shows that the fluid interface position can be controlled by adjusting the strength and the direction of the applied electric field. To demonstrate this concept, results of the interface positions and pressure gradients for flows with different flow rates as the function of the externally applied electric field will be presented.

Using Eq. (4.23), the flow rates of the two liquids are functions of the holdup, ε , and the pressure gradient, $d\bar{p}/d\bar{x}$,

$$\begin{cases} \bar{q}_1 = q_1(\varepsilon, d\bar{p}/d\bar{x}) \\ \bar{q}_2 = q_2(\varepsilon, d\bar{p}/d\bar{x}) \end{cases} \quad (4.40)$$

If the flow rate condition is specified, the system of equations can be solved. Standard Newton-Raphon method is used to solve the holdup and pressure gradient.

Combining Eqs. (4.15a) and (4.15b) yields,

$$\frac{\partial^2 \bar{u}_1}{\partial \bar{z}^2} + \frac{\partial^2 \bar{u}_1}{\partial \bar{y}^2} = \text{Re}G_x \bar{\psi}(\bar{z}, \bar{y}) + \text{Re} \frac{d\bar{p}}{d\bar{x}} \quad (4.41)$$

To investigate the relative importance of the electric force to the pressure gradient on the liquids, a new parameter, S_R , is defined as $S_R = \text{Re}G_x \bar{\zeta}_2 / K$. In Eq. (4.41) the pressure gradient is uniform across the channel while the electroosmotic force is concentrated in the EDL regions close to the channel wall. $1/K$ is the dimensionless thickness of the EDL region. Fig. 4.15 shows the meaning of S_R . The parameter S_R seems as an apparent uniform forces acting on the liquid across the channel.

We first examine the interface positions and pressure gradients for flows with different flow rates through the channel as the function of the externally applied electric field. The results are shown in Figs. 4.16 and 4.17. In the figures, $\beta = 1.5$ and $\chi = 10$ and

Figure 4.15: Schematic representation of the meaning of S_R .

equal volumetric flow rates for the two liquid, $\bar{q}_1 = \bar{q}_2$, are specified. It is obvious that the holdup, ε , remains the same as 0.38 for different volumetric flow rates in the absence of an applied electric field. From Fig 4.16, it is noted that the rate of change of holdup with the applied electric field is lower at high flow rates. This is because under high flow rates, where the pressure gradient is higher, larger applied electric field is required to control the interface position.

Figure 4.18 shows the ability of manipulating the interface position by the externally applied electric field for different viscosity ratio. In these cases, $\bar{q}_1 = \bar{q}_2 = 0.01$ and $\chi = 10$ are specified. The results show that, the lesser viscosity difference between the two fluids, i.e. as viscosity ratio, $\beta = 1$, the larger span is the interface position in the same range of the applied electric field.

The aspect ratios of the channel used for quantitative analysis are generally very big and fall in the range $10 \leq \chi \leq 100$. Fig. 4.19 shows the dependence of the holdup on the applied electric field for different aspect ratio, when $\bar{q}_1 = \bar{q}_2 = 0.01$ and $\beta = 1.5$. For a high aspect ratio, the relationship between the holdup and externally applied electric field becomes nearly linear.

Figure 4.16: Dependence of the holdups of the aqueous solution on the externally applied electric field for different flow rates, $\beta = 1.5$, $\chi = 10$.

Figure 4.17: Dependence of the pressure gradient on the externally applied electric field for different flow rates, $\beta = 1.5$, $\chi = 10$.

Figure 4.18: Dependence of the holdups of the aqueous solution on the externally applied electric field for viscosity ratios, $\bar{q}_1 = \bar{q}_2 = 0.01$, $\chi = 10$.

Figure 4.19: Dependence of the pressure gradient on the externally applied electric field for different aspect ratios, $\beta = 1.5$, $\bar{q}_1 = \bar{q}_2 = 0.01$.

4.5.2 Experimental Validation

To validate the mathematical model, we have conducted experiments for electroosmotic control of the interface for flows of two liquids. The H-shaped microchannel as shown in Fig. 4.20 is fabricated by the adhesive lamination techniques [Wu et al., 2004]. Two PMMA plates are bonded by a layer of double-side adhesive tape (Adhesives Research Inc. Arclad 8120 transfer adhesive) to form a closed microchannel. This adhesive tape defines the depth of the channel. Two platinum electrodes (Adrich-Sigma Singapore) are inserted for the application of the electric field. In the studies, the microchannel has the cross section of $910\mu\text{m} \times 100\mu\text{m}$ and the length of 6.5cm. Aqueous NaCl solution (10^{-4}M) and aqueous glycerol (volume concentration 25%) are introduced side by side in the microchannel by the action of syringe pump. If there is no electric field applied, the interface between two liquids is dependent on the flow rate ratio of two liquids. When different external electric fields are applied, the interface position is also dependent on the magnitude and direction of the external electric field.

Figure 4.20: H-shaped microchannel used in the experiments.

Fluorescence imaging and micro-PIV (micro particle image velocimetry [Nguyen and Wereley, 2002]) measurement are used in this experiment. As shown in Fig. 4.21, it consists of four main components: an illumination system, an optical system, a coupled

Figure 4.21: Schematic of the experimental setup for fluorecence imaging and micro-PIV measurements.

charger device (CCD) camera and a control system. The control system consisting of a peripheral component interface (PCI) card, and its corresponding software, is implemented in a personal computer. The personal computer can control and synchronize all actions related to illumination and image recording.

Two different light sources were used for the two measurements. For the fluorescence imaging measurement, a mercury lamp was used for the illumination. Because of the ability of precise timing and intensity control, a laser beam was used for the micro-PIV measurement. The laser has a wavelength of 532nm and a maximum energy of 160mJ. The two-laser-head system allows the realization of two laser pulses with a very small delay. In the experiments, the mode of double exposures in double frames was used because of the high signal-to-noise ratios and the better quality of the cross-correlation technique.

The optical system was a Nikon inverted microscope (Model ECLIPSE TE2000-S) with a set of epi-fluorescent attachments. There are three optical elements in a filter cube: excitation filter, dichroic mirror and emission filter. Emission filters are used in both measurements to select more specifically the emission wavelength of the sample and to remove traces of excitation light.

An interline transfer CCD camera (Sony ICX 084) was used for recording the images. The resolution of the camera is 640 pixels $\times$ 480 pixels, with 12 bits grayscale. The active area of the CCD sensor is 6.3mm $\times$ 4.8mm. The minimum inter-frame transfer time, and thus the fastest time delay for the two PIV images, is 300ns. To ensure that the CCD camera is working at its optimum temperature of -15°C , a cooling system is integrated in the CCD camera. In the mode of double exposure in double frames, the camera can record two frames of the flow fields and then digitizes them in the same image buffer.

Fluorescent dye (also called Acid Yellow 73) is added in the conducting liquid for the purpose of images collection. When the fluoresein was illuminated by a mercury lamp, an epi-fluorescent attachment of type Nikon B-2A was used (excitation filter for 450-490nm, dichroic mirror for 505nm and an emission filter for 520 nm) to record the

measurement. After recording the images, the interface position between the two fluids was determined by a in-house written MATLAB program.

Figure 4.22 shows the comparison between the analytical results and the experimental results of the interface positions for different applied electric fields. In calculation, the reference velocity $V = 1.13 \times 10^{-3} \text{m/s}$ and the reference length $L = 910 \mu\text{m}$. The viscosity of NaCl solution and aqueous glycerol is $1.12 \times 10^{-3} \text{N}\cdot\text{s}/\text{m}^2$ and $1.8 \times 10^{-3} \text{N}\cdot\text{s}/\text{m}^2$, respectively. Under these conditions, the dimensionless flow rate is 0.0148 for 0.05mL/h and 0.0296 for 0.1mL/h. The zeta potential between PMMA and NaCl solution is measured by electroosmotic mobility method. The results show that the zeta potential at the channel is -24.4mV. Thus when the applied electric field is 1000V/m, the value of S_R is 268.64. From Fig. 4.22, the comparison shows that the proposed analytical model can predict the interface position relatively well.

4.5.3 Velocity Profiles

The PIV measurements use an epi-fluorescent attachment of type Nikon G-2E/C. The measurement reported in this experiment was carried out with a 4×objective. With a CCD sensor size of 6.3mm×4.8mm, the size of an image pixel is $2.475 \mu\text{m}$ and the size of the measured area is $1548 \mu\text{m} \times 1188 \mu\text{m}$.

The seeding particles used in experiments are Duke red particles (Duke scientific Co.). The diameter of the particle can be chosen from several hundreds of nanometers to several microns. The particles have a maximum excitation wavelength of 540 nm (green, very close to the characteristic wavelength of Nd: YAG) and a maximum emission wavelength of 610 nm (red).

Two 30 mJ laser pulses with a delay time of 3.5 ms were used as illumination sources. The integration area is 32 pixels × 32 pixels. The measurement was taken at 1 mm downstream of the entrance of the channel, where the stable velocity field is established.

The total measured velocity of a seed particle in the high EO liquid, $u_{1,\text{meas}}$, is a linear

(a) $q_1 = q_2 = 0.05 \text{ mL/h}$

(b) $q_1 = q_2 = 0.1 \text{ mL/h}$

Figure 4.22: Comparison of the holdups between calculated and experimental results.

superposition of the pressure-driven, u_1^P , electroosmotic, u_1^E , electrophoretic, u_1^{EPH} , and Brownian components motion, u_1^B . It can be expressed as

$$u_1^{\text{meas}} = u_1^P + u_1^E + u_1^{EPH} + u_1^B \quad (4.42a)$$

As the EOF in glycerol is not considered, The total measured velocity of a seed particle in the non-aqueous liquid, u_2^{meas} , is a linear superposition of the pressure driven, u_2^P , component influenced by electroosmotic flow in the conducting liquid, u_2^E , and Brownian components motion, u_2^B , expressed by

$$u_2^{\text{meas}} = u_2^P + u_2^E + u_2^B \quad (4.42b)$$

The last term in Eq. (4.42b) is the temporally average velocity of the particle due to Brownian motion during the interval of observation. Its contribution is minimized by ensemble average spatially resolved velocities over several realizations [Devasenathipathy et al., 2002]. The electrophoresis velocity is a function of the particle's surface zeta potential, ζ_P , in the solution, expressed as

$$u_1^{EPH} = \frac{\zeta_P \epsilon_r \epsilon_0 E_x}{\mu_1} \quad (4.43)$$

The particle's zeta potential used is -15.9mV as reported by Yan [2005]. Thus, the measured velocities $u_1^E + u_1^P$ and $u_2^E + u_2^P$ are obtained.

(a) $S_R = -413.3$, ($E_x = -3076.9 \text{ V/m}$)

(b) $S_R = 0$

Figure 4.23: Comparison between theoretical and experimental velocity profiles, (continued).

(c) $S_R = 413.3$, ($E_x = 3076.9 \text{ V/m}$)

(d) $S_R = 826.6$, ($E_x = 6135.8 \text{ V/m}$)

Figure 4.23: Comparison between theoretical and experimental velocity profiles.

Comparison between the theoretical solution and the measured velocity profiles under different applied electric fields is shown in Fig. 4.23. The flow rate is 0.1mL/h. Reasonably good agreement is obtained. In the theoretical prediction, a relatively sharp transverse gradient occurs at the interface, as the model assumes no diffusion between liquids. In fact, glycerol is miscible in water; therefore, there exists a diffusion region in experimental results. From Fig. 4.23, it is also observed that the analytical model underestimates the velocity. This is because that the Debye-Hückel linear approximation approach was made when calculating the potential distribution in Eq. (4.1) and the electroosmotic force in Eq. (4.15a). For more details of analysis, non-linear equations should be considered.

Chapter 5

Numerical Analysis

In the previous chapter, analytical solutions of the fully developed laminar flow of two liquids under the combined effects of pressure gradient, electroosmosis and surface charges at the liquid-liquid interface were presented. A planar interface is assumed. In the entrance region, the interface between the two liquids evolves along the flow direction. The velocity profile and interface position at every section varies. The liquid-liquid interface is non-planar. Due to the curvature of the interface and the presence of the surface charges in electrokinetic phenomena, pressure jump and stress jump across the interface.

In this chapter, a level set method with jump conditions across the interface will be presented. First, we obtain a derivation including the surface tension and surface charge terms and the associated pressure and stress jumps. Furthermore, a novel discretization method is developed to solve these jump conditions. It is following the modified SIMPLER algorithm and some numerical experiments to verify this method.

5.1 Implementation of Surface Tension and Surface Charges

Here we consider not only the surface tension but also the effect of surface charges between the two fluids. The interaction of the applied electric field and the surface charge is difficult to convert into a volume body force by continuous surface method. Therefore, the jump condition expression of Navier-Stokes equation for two-liquid flow is used. The presences of surface tension and surface charge are written in jumps of the pressure and stress.

The jump conditions with surface charges and surface tension in normal and tangential direction are

$$[[p]] = \kappa\sigma + [[T']] : \mathbf{nn} + \rho_q^s [[\mathbf{E}]]_+ \cdot \mathbf{n} \quad (3.27a)$$

$$\nabla_s \sigma + \mathbf{n} \cdot [[\mathbf{T}']] \cdot (\mathbf{I} - \mathbf{nn}) - \rho_q^s \mathbf{E} \cdot (\mathbf{I} - \mathbf{nn}) = 0 \quad (3.27b)$$

The velocities are continuous across the interface,

$$[[u]] = [[v]] = 0 \quad (5.2)$$

as well as their tangential derivatives

$$[[\nabla u \cdot \mathbf{t}]] = [[\nabla v \cdot \mathbf{t}]] = 0 \quad (5.3)$$

Here $\mathbf{t} = (\mathbf{I} - \mathbf{nn})$ is the tangential vector in two dimension. Specially, from the normal vector $\mathbf{n} = (n_1, n_2)$, we can define the tangential vector $\mathbf{t} = (t_1, t_2)$ as

$$\begin{cases} t_1 = n_2 \\ t_2 = -n_1 \end{cases} \quad (5.4)$$

Therefore, from the continuity equation,

$$\nabla \cdot \mathbf{v} = (\nabla u \cdot \mathbf{n}, \nabla v \cdot \mathbf{n}) \cdot \mathbf{n} + (\nabla u \cdot \mathbf{t}, \nabla v \cdot \mathbf{t}) \cdot \mathbf{t} = 0 \quad (5.5)$$

One obtains

$$[(\nabla u \cdot \mathbf{n}, \nabla v \cdot \mathbf{n}) \cdot \mathbf{n}] = 0 \quad (5.6)$$

However, the jump in pressure across the interface can be rewritten in the form easy for numerical analysis

$$[[p]] = 2 [[\mu]] (\nabla u \cdot \mathbf{n}, \nabla v \cdot \mathbf{n}) \cdot \mathbf{n} + \kappa \sigma + \rho_q^s \mathbf{E} \cdot \mathbf{n} \quad (5.7)$$

If the surface tension is independent of position, the jump in tangential stress, Eq. (3.27b), is rewritten as

$$[[\mu (\nabla u \cdot \mathbf{n}, \nabla v \cdot \mathbf{n}) \cdot \mathbf{t} + \mu (\nabla u \cdot \mathbf{t}, \nabla v \cdot \mathbf{t}) \cdot \mathbf{n}]] + \rho_q^s \mathbf{E} \cdot \mathbf{t} = 0 \quad (5.8)$$

Substituting Eq. (5.5) into Eq. (5.8), we obtain

$$[[\mu (\nabla u \cdot \mathbf{n}, \nabla v \cdot \mathbf{n}) \cdot \mathbf{t}]] = - [[\mu]] (\nabla u \cdot \mathbf{t}, \nabla v \cdot \mathbf{t}) \cdot \mathbf{n} - \rho_q^s \mathbf{E} \cdot \mathbf{t} \quad (5.9)$$

Eq. (5.9) can be rewritten as

$$\begin{aligned} \begin{pmatrix} [[\mu u_x]] & [[\mu u_y]] \\ [[\mu v_x]] & [[\mu v_y]] \end{pmatrix} &= [[\mu]] \begin{pmatrix} \nabla u \\ \nabla v \end{pmatrix} \begin{pmatrix} \mathbf{0} \\ \mathbf{t} \end{pmatrix}^T \begin{pmatrix} \mathbf{0} \\ \mathbf{t} \end{pmatrix} + [[\mu]] \mathbf{n}^T \mathbf{n} \begin{pmatrix} \nabla u \\ \nabla v \end{pmatrix} \mathbf{n}^T \mathbf{n} \\ &\quad - [[\mu]] \begin{pmatrix} \mathbf{0} \\ \mathbf{t} \end{pmatrix}^T \begin{pmatrix} \mathbf{0} \\ \mathbf{t} \end{pmatrix} \begin{pmatrix} \nabla u \\ \nabla v \end{pmatrix}^T \mathbf{n}^T \mathbf{n} - \begin{pmatrix} \mathbf{n} \\ \mathbf{t} \end{pmatrix}^T \begin{pmatrix} 0 & 0 \\ \rho_q^s \mathbf{E} \cdot \mathbf{t} & 0 \end{pmatrix} \begin{pmatrix} \mathbf{n} \\ \mathbf{t} \end{pmatrix} \end{aligned} \quad (5.10)$$

The Capillary number Ca is defined as

$$\text{Ca} = \frac{\mu V_{\text{ref}}}{\sigma} \quad (5.11)$$

Using $\rho_q^s = \epsilon \frac{k_b T}{z_0 e L_{\text{ref}}} \bar{\rho}_q^s$ and $\mathbf{E} = \frac{k_b T}{z_0 e L_{\text{ref}}} \bar{\mathbf{E}}$, the above Eq. (5.7) is normalized as

$$[\bar{p}] = \frac{2}{\text{Re}} [\bar{\mu}] (\nabla \bar{u} \cdot \mathbf{n}, \nabla \bar{v} \cdot \mathbf{n}) \cdot \mathbf{n} + \frac{\bar{\kappa}}{\text{ReCa}} + G_s^m \bar{\rho}_q^s \bar{\mathbf{E}} \cdot \mathbf{n} \quad (5.12a)$$

where $\kappa = \bar{\kappa}/L_{\text{ref}}$ and $G_s^m = \frac{\epsilon}{\rho_{\text{ref}} V_{\text{ref}}^2} \left(\frac{k_b T}{z_0 e L_{\text{ref}}} \right)^2$. Eq. (5.10) becomes

$$\begin{aligned} \begin{pmatrix} [\bar{\mu} \bar{u}_x] & [\bar{\mu} \bar{u}_y] \\ [\bar{\mu} \bar{v}_x] & [\bar{\mu} \bar{v}_y] \end{pmatrix} &= [\bar{\mu}] \begin{pmatrix} \nabla \bar{u} \\ \nabla \bar{v} \end{pmatrix} \begin{pmatrix} \mathbf{0} \\ \mathbf{t} \end{pmatrix}^T \begin{pmatrix} \mathbf{0} \\ \mathbf{t} \end{pmatrix} + [\bar{\mu}] \mathbf{n}^T \mathbf{n} \begin{pmatrix} \nabla \bar{u} \\ \nabla \bar{v} \end{pmatrix} \mathbf{n}^T \mathbf{n} \\ &\quad - [\bar{\mu}] \begin{pmatrix} \mathbf{0} \\ \mathbf{t} \end{pmatrix}^T \begin{pmatrix} \mathbf{0} \\ \mathbf{t} \end{pmatrix} \begin{pmatrix} \nabla \bar{u} \\ \nabla \bar{v} \end{pmatrix}^T \mathbf{n}^T \mathbf{n} - \begin{pmatrix} \mathbf{n} \\ \mathbf{t} \end{pmatrix}^T \begin{pmatrix} 0 & 0 \\ \bar{\rho}_q^s (\bar{\mathbf{E}} \cdot \mathbf{t}) G_s^t & 0 \end{pmatrix} \begin{pmatrix} \mathbf{n} \\ \mathbf{t} \end{pmatrix} \end{aligned} \quad (5.12b)$$

where $G_s^t = \frac{\epsilon}{L_{\text{ref}} \mu_{\text{ref}} U_{\text{ref}}} \left(\frac{k_b T}{z_0 e} \right)^2$. It can be seen that the terms on the right hands of Eq. (5.12) are continuous. Therefore, it is easy to be implemented in numerical analysis.

5.2 Level Set Method

5.2.1 Level set function

The intrinsic definition of the surface is defined by Eq. (3.1). In the solution of the function $F(\mathbf{r}, t)$, any convenient reference value can be assigned to the interface, such as the concentration, density etc. The values of $F(\mathbf{r}, t)$ at all node points are then calculated

based on the reference value at the interface. The level set function, ϕ is defined such that $F(\mathbf{r}, t)$ is the normal distance from the local node to the interface. The value of ϕ is set to zero at the interface. Therefore, the interface between two liquids is identified by Osher and Fedkiw [2002]

$$\phi(\mathbf{x}, t) = 0 \quad (5.13)$$

Figure 5.1: The schematic of level set function

As a result, ϕ has opposite signs in the two liquids as shown in Fig. 5.1. It is the distance function which satisfies $|\nabla \phi| = 1$. The evolution of ϕ is

$$\frac{\partial \phi}{\partial t} + \mathbf{v} \cdot \nabla \phi = 0 \quad (5.14)$$

As time increases and the interface propagates, the level set function ϕ evolves so that the embedded motion of interface is still given by $\phi(\mathbf{x}, t) = 0$.

Geometric properties of the interface can easily be determined from the level set function [Osher and Fedkiw, 2000], ϕ . The normal vector at any point of the front is given by

$$\mathbf{n} = \frac{\nabla \phi}{|\nabla \phi|}$$

and the curvature of the interface is

$$\kappa = -\nabla \cdot \mathbf{n}$$

5.2.2 Redistribution

In the process of numerical simulations, ϕ must remain a distance function. However, this can only be ensured at the beginning of the iteration process where the location of the interface is assumed and the values of ϕ at all nodes are specified. During the iteration process, the value of ϕ are calculated using Eq. (5.14). Although the interface is still represented by the reference value, the other values of ϕ might not be the distances from the interface. As a result, another scalar variable is defined and solved. This variable must be a distance function and has the same interface value as ϕ . The 'steady-state' solution of ξ in Eq. (5.15) satisfies above requirements [Osher and Fedkiw, 2000],

$$\frac{\partial \xi}{\partial \tau} = \text{sign}(\phi)(1 - |\nabla \xi|) \quad (5.15)$$

In Eq. (5.15), τ is a *pseudo* time for the variable ξ . Eq. (5.15) is subjected to the following initial condition,

$$\xi(\mathbf{x}, 0) = \phi(\mathbf{x}, t) \quad (5.16)$$

It is clear from Eq. (5.15) that the 'steady-state' solution satisfies $|\nabla \xi| = 1$. Thus, it is a distance function. The initial value, Eq. (5.16), ensures that the interface value of ξ is identical to the interface value of ϕ . As the result, the "steady-state" values of ξ are distances from the local location to the interface.

Although, Eq. (5.16) ensures ξ and thus ϕ as the distance function, it suffers a significant drawback. It dose *not* ensure the conservation of mass of the various phases. To ensure mass conservation at each cross-section, a local mass correction factor is

defined and an additional equation is solved. This is written as [Yap et al., 2005]

$$\frac{\partial \xi'}{\partial \tau'} = \dot{m}_{\text{cor}} \quad (5.17)$$

In Eq. (5.17), τ' and $\dot{m}_{\text{cor}}$ are pseudo-time and mass conservation factor, respectively.

The local mass correction factor is

$$\dot{m}_{\text{cor}} = \text{sign}(\phi_{\text{ref}}) \frac{(\dot{m}_d - \dot{m}_c)}{\dot{m}_d} \quad (5.18)$$

where $\dot{m}_d$ and $\dot{m}_c$ are the desired mass flowrate and the most current mass flowrate of the reference liquid, respectively. $\text{sign}(\phi_{\text{ref}})$ is the sign of the level set function of the reference liquid.

5.3 Numerical Scheme for Jump Conditions

In this section, we consider Poisson equation on a domain including an interface. The boundary conditions are discontinuous across the interface. Finite difference method is developed for jump conditions [Kang et al., 2000; Liu et al., 2000].

5.3.1 One dimensional case

We consider the one dimensional Poisson equation

$$(\beta u_x)_x = f(x) \quad (5.19)$$

in a Cartesian computational domain Ω , with the jump conditions, $[[u]]_{\Gamma} = a(x)$ and $[[\beta u_n]]_{\Gamma} = b(x)$ at the interface, Γ , as shown in Fig. 5.2

Figure 5.2: The schematic of numerical method in 1D

The general equation, (5.19) is, normally, discretized by

$$\frac{\beta_{E+1/2} \left(\frac{u_E - u_P}{\Delta x} \right) - \beta_{W+1/2} \left(\frac{u_P - u_W}{\Delta x} \right)}{\Delta x} = f(x_P) \quad (5.20)$$

However, if the interface is between P and E, the difference scheme is not defined rightly across the interface. The discontinuity should be integrated in the numerical scheme. We define u^- and u^+ , which satisfy

$$\begin{cases} u^+ - u^- = a_\Gamma \\ \beta^+ \left(\frac{u_E - u^+}{\Delta x} \right) - \beta^- \left(\frac{u^- - u_P}{\Delta x} \right) = b_\Gamma \end{cases} \quad (5.21)$$

Solving above equations, we have

$$\begin{cases} u^+ = \frac{\beta^+ \theta u_E + \beta^- u_P (1 - \theta) - b_\Gamma \theta (1 - \theta) \Delta x + \beta^- (1 - \theta) a_\Gamma}{\beta^+ \theta + \beta^- (1 - \theta)} \\ u^- = \frac{\beta^+ \theta u_E + \beta^- u_P (1 - \theta) - b_\Gamma \theta (1 - \theta) \Delta x - \beta^+ \theta a_\Gamma}{\beta^+ \theta + \beta^- (1 - \theta)} \end{cases} \quad (5.22)$$

Therefore, we can define

$$\begin{cases} \beta^+ \left(\frac{u_E - u^+}{\Delta x} \right) = \hat{\beta} \left(\frac{u_E - u_P}{\Delta x} \right) + \frac{\hat{\beta} b_\Gamma \theta}{\beta^-} - \frac{\hat{\beta} a_\Gamma}{\Delta x} \\ \beta^- \left(\frac{u^- - u_P}{\Delta x} \right) = \hat{\beta} \left(\frac{u_E - u_P}{\Delta x} \right) - \frac{\hat{\beta} b_\Gamma (1 - \theta)}{\beta^+} - \frac{\hat{\beta} a_\Gamma}{\Delta x} \end{cases} \quad (5.23)$$

where $\theta = \frac{|\phi_P|}{|\phi_P| + |\phi_E|}$ and $\hat{\beta} = \frac{\beta^+ \beta^- (|\phi^+| + |\phi^-|)}{\beta^+ |\phi^-| + \beta^- |\phi^+|}$

Then we have the finite difference scheme as

$$\frac{\beta^- \left(\frac{u^- - u_P}{\Delta x} \right) - \beta_{W+1/2} \left(\frac{u_P - u_W}{\Delta x} \right)}{\Delta x} = f(x_P) \quad (5.24)$$

we write this as

$$a_P u_P = a_E u_E + a_W u_W + b$$

where $a_E = \hat{\beta}$, $a_W = \beta_{W+1/2}$, $a_P = a_E + a_W$ and $b = -\frac{\hat{\beta} b_\Gamma (1 - \theta)}{\beta^+} - \frac{\hat{\beta} a_\Gamma}{\Delta x}$

5.3.2 Two dimensional case

We consider the two dimensional Poisson equation

$$(\beta u_x)_x + (\beta u_y)_y = f(x, y) \quad (5.25)$$

with interface jump conditions, $[[u]]_\Gamma = a(x)$ and $[[\beta u_n]]_\Gamma = b(x)$

For the 2D scheme as shown in Fig. 5.3, the method developed previously is applied.

The discretization of Eq. (5.25) is

$$a_P u_P = a_E u_E + a_W u_W + a_N u_N + a_S u_S + b$$

Depending on the interface position, the coefficient a_E , a_W , a_N , a_S , a_P and b can be expressed as

1. Coefficient $a_E = \frac{k_e \Delta y}{(\delta x)_e}$ and the parameter k_e is determined as the following:
if $\phi_E \phi_P > 0$, the interface is not allocated between P and E, then

$$k_e = \left[\frac{(\delta x)_e^-}{(\delta x)_e k_P} + \frac{(\delta x)_e^+}{(\delta x)_e k_E} \right]^{-1}$$

Figure 5.3: The schematic of numerical method in 2D

if $\phi_E \phi_P < 0$, the interface is located between P and E, then define $\phi^- = \phi_P$, $\phi^+ = \phi_E$, $k^- = k_P$, $k^+ = k_E$, $\theta = |\phi^-| / (|\phi^-| + |\phi^+|)$, hence

$$k_e = \hat{k} = \frac{\beta^+ \beta^- (|\phi^+| + |\phi^-|)}{\beta^+ |\phi^-| + \beta^- |\phi^+|}$$

2. Coefficient $a_W = \frac{k_w \Delta y}{(\delta x)_w}$ and the parameter k_w is determined as the following:

if $\phi_W \phi_P > 0$, the interface is not allocated between P and W, then

$$k_w = \left[\frac{(\delta x)_w^-}{(\delta x)_w k_P} + \frac{(\delta x)_w^+}{(\delta x)_w k_W} \right]^{-1}$$

if $\phi_W \phi_P < 0$, the interface is located between P and W, then define $\phi^- = \phi_W$, $\phi^+ = \phi_P$, $k^- = k_W$, $k^+ = k_P$, $\theta = |\phi^-| / (|\phi^-| + |\phi^+|)$, hence

$$k_w = \hat{k} = \frac{\beta^+ \beta^- (|\phi^+| + |\phi^-|)}{\beta^+ |\phi^-| + \beta^- |\phi^+|}$$

3. Coefficient $a_N = \frac{k_n \Delta y}{(\delta x)_n}$ and the parameter k_n is determined as the following:
if $\phi_N \phi_P > 0$, the interface is not located between P and N, then

$$k_n = \left[\frac{(\delta y)_n^-}{(\delta y)_n k_P} + \frac{(\delta y)_n^+}{(\delta y)_n k_N} \right]^{-1}$$

if $\phi_N \phi_P < 0$, the interface is located between P and N, then define $\phi^- = \phi_P$, $\phi^+ = \phi_N$, $k^- = k_P$, $k^+ = k_N$, $\theta = |\phi^-| / (|\phi^-| + |\phi^+|)$, hence

$$k_n = \hat{k} = \frac{\beta^+ \beta^- (|\phi^+| + |\phi^-|)}{\beta^+ |\phi^-| + \beta^- |\phi^+|}$$

4. Coefficient $a_S = \frac{k_s \Delta y}{(\delta x)_s}$ and the parameter k_s is determined as the following:
if $\phi_S \phi_P > 0$, the interface is not located between P and S, then

$$k_s = \left[\frac{(\delta y)_s^-}{(\delta y)_s k_P} + \frac{(\delta y)_s^+}{(\delta y)_s k_S} \right]^{-1}$$

if $(\phi_S > 0 \ \& \ \phi_P < 0)$ or $(\phi_S < 0 \ \& \ \phi_P > 0)$, the interface is located between P and S, then define $\phi^- = \phi_S$, $\phi^+ = \phi_P$, $k^- = k_S$, $k^+ = k_P$, $\theta = |\phi^-| / (|\phi^-| + |\phi^+|)$, hence

$$k_s = \hat{k} = \frac{\beta^+ \beta^- (|\phi^+| + |\phi^-|)}{\beta^+ |\phi^-| + \beta^- |\phi^+|}$$

5. Coefficient $a_P = a_E + a_W + a_N + a_S + a_P^0 - S_P \delta x \delta y$

6. Coefficient $b = S_c \Delta x \Delta y + a_P^0 u_P^0 +$

- if $\phi_W \phi_P < 0$: $\left(-\frac{\hat{k} a_\Gamma}{(\delta x)_e} - \frac{\hat{k} b_\Gamma (1 - \theta)}{k^+} \right)$
- if $\phi_W \phi_P > 0$: $\left(+\frac{\hat{k} a_\Gamma}{(\delta x)_w} - \frac{\hat{k} b_\Gamma (1 - \theta)}{k^-} \right)$
- if $\phi_N \phi_P > 0$: $\left(-\frac{\hat{k} a_\Gamma}{(\delta y)_n} - \frac{\hat{k} b_\Gamma (1 - \theta)}{k^+} \right)$

- if $\phi_S \phi_P > 0$: $\left(+\frac{\hat{k}a_\Gamma}{(\delta y)_s} - \frac{\hat{k}b_\Gamma(1-\theta)}{k^-} \right)$

5.4 SIMPLER Algorithm with Jump Interface Condition

Now we incorporate the numerical scheme developed in section 5.3 into the SIMPLER algorithm [Patankar, 1980].

5.4.1 Velocity equation

The momentum equation of u is written as

$$\frac{\partial(\rho u)}{\partial t} + \nabla \cdot (\mathbf{v}u) = -\frac{\partial p}{\partial x} + \nabla \cdot (\mu \nabla u) \quad (5.26)$$

This equation is rewritten as

$$\frac{\partial(\rho u)}{\partial t} + \nabla \cdot (\mathbf{v}u - \mu \nabla u) = -\frac{\partial p}{\partial x} \quad (5.27)$$

The discretization equation of Eq. (5.27) is

$$a_e u_e = \sum a_{nb} u_{nb} + b + (p_P - p_E) A_e \quad (5.28a)$$

Similarly, the discretization equation of v is

$$a_n v_n = \sum a_{nb} v_{nb} + b + (p_P - p_N) A_n \quad (5.28b)$$

Velocity is continuous across the interface, the term $\mathbf{v}u$ in Eqs. (5.26) and (5.27) is computed by the method presented by Patankar [1980]. The jump in stress $\mu \nabla u$ across the interface, however, should be computed by the method presented above. From Eq.

(5.10), jump in normal stress across the interface

$$[[\mu u_n]] = [[\mu u_x]] n_1 + [[\mu u_y]] n_2 \quad (5.29a)$$

$$[[\mu v_n]] = [[\mu v_x]] n_1 + [[\mu v_y]] n_2 \quad (5.29b)$$

If the interface is at a position between P and E

$$[[p]] = p_E - p_P \quad (5.30)$$

the first derivative of p is,

$$\frac{\partial p}{\partial x} \doteq \frac{p_E - p_P}{(\delta x)_e} \quad (5.31)$$

will be replaced by

$$\frac{\partial p}{\partial x} \doteq \frac{(p_E - [[p]]) - p_P}{(\delta x)_e} \quad (5.32)$$

Therefore the discretization Eq. (5.28) is replaced by

$$a_e u_e = \sum a_{nb} u_{nb} + b + (p_P - p_E + \hat{p}_e) \Delta y \quad (5.33a)$$

and

$$a_n v_n = \sum a_{nb} v_{nb} + b + (p_P - p_N + \hat{p}_n) \Delta x \quad (5.33b)$$

where $\hat{p}_e$ is the pressure jump across the interface between P and E, $\hat{p}_n$ is the pressure jump across the interface between P and N.

5.4.2 Pressure and velocity corrections

The momentum equations can be solved only when the pressure field is given or is somehow estimated. Unless the correct pressure field is employed, the resulting velocity field will not satisfy the continuous equation. Such an imperfect velocity field based on a guessed pressure field p^* will be denoted by u^* and v^* . This "starred" velocity field

will result from the solution of the following discretization equations [Patankar, 1980],

$$a_e u_e^* = \sum a_{nb} u_{nb}^* + b + (p_P^* - p_E^* + \hat{p}_e) \Delta y \quad (5.34a)$$

and

$$a_n^* v_n^* = \sum a_{nb} v_{nb}^* + b + (p_P^* - p_N^* + \hat{p}_n) \Delta x \quad (5.34b)$$

Let us propose that the correct pressure p is obtained from

$$p = p^* + p' \quad (5.35)$$

where p' is called the pressure correction. The corresponding velocity corrections u' and v' can be introduced in a similar manner:

$$u = u^* + u' \quad (5.36)$$

and

$$v = v^* + v' \quad (5.37)$$

In we subtract Eq. (5.34a) from (5.33a), we have

$$a_e u_e' = \sum a_{nb} u_{nb}' + (p_P' - p_E') \Delta y \quad (5.38)$$

we drop the term $\sum a_{nb} u_{nb}'$ and get

$$u_e' = d_e (p_P' - p_E')$$

where $d_e = \frac{\Delta y}{a_e}$. Therefore, we have

$$u_e = u_e^* + d_e (p_P' - p_E') \quad (5.39a)$$

Similarly,

$$v_n = v_n^* + d_n(p'_P - p'_N) \quad (5.39b)$$

5.4.3 Pressure-correction equation

The continuity equation is

$$\frac{\partial \rho}{\partial t} + \frac{\partial(\rho u)}{\partial x} + \frac{\partial(\rho v)}{\partial y} = 0 \quad (5.40)$$

The discretization form of Eq. (5.40) is

$$\frac{(\rho_P - \rho_P^0)\Delta x \Delta y}{\Delta t} + [(\rho u)_e - (\rho u)_w] \Delta y + [(\rho u)_n - (\rho u)_s] \Delta x = 0 \quad (5.41)$$

Substituting Eq. (5.39) yields the discretization equation for p'

$$a_P p'_P = a_E p'_E + a_W p'_W + a_N p'_N + a_S p'_S + b \quad (5.42)$$

where

$$a_E = \rho_e d_e \Delta y \quad (5.43a)$$

$$a_W = \rho_w d_w \Delta y \quad (5.43b)$$

$$a_N = \rho_n d_n \Delta x \quad (5.43c)$$

$$a_S = \rho_s d_s \Delta x \quad (5.43d)$$

and

$$b = \frac{(\rho_P^0 - \rho_P)\Delta x \Delta y}{\Delta t} + [(\rho u^*)_w - (\rho u^*)_e] \Delta y + [(\rho u^*)_s - (\rho u^*)_n] \Delta x \quad (5.43e)$$

5.4.4 Pressure equation

The momentum equations (5.33a) and (5.33b) are written as

$$u_e = \frac{\sum a_{nb}u_{nb} + b}{a_e} + d_e(p_P - p_E + \hat{p}_e) \quad (5.44a)$$

$$u_n = \frac{\sum a_{nb}v_{nb} + b}{a_n} + d_n(p_P - p_N + \hat{p}_n) \quad (5.44b)$$

Now we define a pseudo-velocity $\hat{u}_e$ by

$$\tilde{u}_e = \frac{\sum a_{nb}u_{nb} + b}{a_e} + d_e\hat{p}_e \quad (5.45)$$

Eq. (5.44b) becomes

$$u_e = \tilde{u}_e + d_e(p_P - p_E) \quad (5.46)$$

Similarly, if we define

$$\tilde{v}_n = \frac{\sum a_{nb}v_{nb} + b}{a_n} + d_n\hat{p}_n \quad (5.47)$$

then

$$v_n = \tilde{v}_n + d_n(p_P - p_N) \quad (5.48)$$

Then we can derive the pressure equation,

$$a_P p_P = a_E p_E + a_W p_W + a_N p_N + a_S p_S + b \quad (5.49a)$$

where $a_E = \rho_e d_e \Delta y$, $a_W = \rho_w d_w \Delta y$, $a_N = \rho_n d_n \Delta x$, $a_S = \rho_s d_s \Delta x$ and

$$b = \frac{(\rho_P^0 - \rho_P) \Delta x \Delta y}{\Delta t} + [(\rho \tilde{u})_w - (\rho \tilde{u})_e] \Delta y + [(\rho \tilde{u})_s - (\rho \tilde{u})_n] \Delta x \quad (5.49b)$$

5.4.5 SIMPLER algorithm

1. Start with a guessed velocity field and interface location.

2. Calculate the normal distances for all nodes from the interface.
3. Calculate the coefficients for the momentum equations and hence calculate $\tilde{u}$ and $\tilde{v}$ from Eqs. (5.45) and (5.47).
4. Calculate the coefficients for pressure equation Eq. (5.49), and solve it to obtain the pressure field.
5. Treating this pressure field as p^* , solve the momentum Eqs. (5.33a) and (5.33b) to obtain u^* and v^* .
6. Calculate the mass source b by Eq. (5.43e) and hence solve the p' equation.
7. Correct the velocity field by use of Eqs. (5.36) and (5.37), but do not correct the pressure.
8. Return to step 2 and repeat until convergence.

5.5 Numerical Analysis of Two-liquid Stratified flow

In this section, we tested the numerical model for two-liquid stratified flow between two parallel plates of length L separated by a distance H . We simulate two immiscible liquids: liquid 1 at the lower section and liquid 2 at the upper section of the channel as shown in Fig. 1.1(without applied electric field). For a given set of viscosity ratio, mass flow rate ratio and the inlet ‘thickness’ δ_{in} of liquid 1, the interface between two liquids evolves along the flow direction. The velocity profile and interface position at every section change. In fully-developed region, the velocity profile and interface position δ become independent of the axial coordinate.

5.5.1 Two immiscible liquids with the same properties

In this problem, two immiscible liquids with the same densities $\bar{\rho}_1 = \bar{\rho}_2 = 1$ and viscosities $\bar{\mu}_1 = \bar{\mu}_2 = 1$ flow between two parallel plates of $L/H = 2$ is considered. The

inlet interface is set to $\delta_{\text{in}} = 0.7$. The flowrates of two liquids are equal, $\bar{q}_1 = \bar{q}_2 = 0.01$. Fig. 5.4 shows the interface and the velocity profiles at five streamwise locations, when $\text{Ca} = 10$ and $\text{Re} = 0.1$. Due to the same viscosity, at the outlet, the flow is fully-developed and the interface is at 0.5. It can be seen that the fully developed velocity profile is identical to the exact solution presented in Chapter 5.

The effect of surface tension given in term of Ca and the interface evolution is shown in Fig. 5.5. The limiting case of $\text{Ca} = \infty$ corresponds to the situation of no surface tension effect. As expected, once fully-developed flow is reached, the interface converges to the same value irrespective of the Ca .

Figure 5.4: Evolution of velocity and interface profiles along x/H when $\text{Ca} = 10$ and $\text{Re} = 0.1$.

Figure 5.6 shows the pressure jump across the interface. As the two immiscible fluids with the same viscosities, $\mu_1 = \mu_2$, the pressure jump is due to the effect of curvature, $[[p]] = \kappa\sigma$. That there is no pressure jump for $\text{Ca} = \infty$ shows no surface tension effect. For $\text{Ca} = 10$ (Fig. 5.6(a)), the pressure jump varies along x/H , at the fully-developed region, the interface is 'flat', the pressure jump disappears.

Figure 5.5: Evolution of interface profiles along x/H for different Ca .

5.5.2 Two immiscible liquids with different properties

In this example, two immiscible liquids with same density $\bar{\rho}_1 = \bar{\rho}_2 = 1$ but with different viscosities $\bar{\mu}_1 = 1$ and $\bar{\mu}_2 = 3$ flow between two parallel plates of $L/H = 2$ is considered. The inlet interface is set to $\delta_{in} = 0.7$. The flowrates of two liquids are equal, $\bar{q}_1 = \bar{q}_2 = 0.01$. The interface evolutions are shown in Fig.5.8. Fig. 5.7 shows the interface and the velocity profiles at five streamwise locations, when $Ca = 10$ and $Re = 0.1$. A similar to the case where the properties of both fluids are the same is obtained.

Figure 5.9 shows the pressure jump across the interface for immiscible liquids with different viscosity ratio, $\mu_2/\mu_1 = 3$. Fig. 5.9(a) shows that for flow without surface tension $Ca = \infty$, pressure jump exists across the interface, $[[p]] = 2[[\mu]](\nabla \mathbf{u} \cdot \mathbf{n}, \nabla \mathbf{v} \cdot \mathbf{n})$. The magnitude of the pressure jump depends on the velocity derivatives of the two fluids and values of their viscosities.

For $Ca = 10$ (Fig. 5.9(b)), the pressure jump depends on the combined effects of surface tension, velocity derivatives and viscosity of the two fluids. In the fully developed region, no pressure jump across the interface as the curvature and velocity derivatives vanishes.

Figure 5.6: Pressure distributions for two immiscible liquids with same properties.

Figure 5.7: Evolution of velocity and interface profiles along x/H when $Ca = 10$ and $Re = 0.1$.

Figure 5.8: Evolution of interface profiles along x/H for different Ca .

(a) Pressure jump across the interface due to the difference of two-liquid viscosities, $Ca = \infty$ and $Re = 0.1$.

(b) Pressure jump across the interface due to the difference of two-liquid viscosities and surface tension, $Ca = \infty$ and $Re = 0.1$.

Figure 5.9: Pressure distributions for two immiscible liquids with different properties.

5.6 Numerical Analysis of Two-liquid Stratified Electroosmotic Flow

5.6.1 Governing Equations

Figure 1.1 shows the schematic of the problem. The microchannel is filled with two (an aqueous and a non-aqueous) immiscible fluids. When an electric field is applied across the channel, the aqueous solution is driven by electroosmosis. The aqueous solution then drags the non-aqueous liquid by the interfacial viscous force causing it to flow along the microchannel.

The steady, incompressible continuity and momentum equations for Newtonian fluids for the two-fluid flow problem are written as

$$\nabla^2 \bar{\psi} = K^2 \sinh(\bar{\psi}) \quad (3.30a)$$

$$\bar{\rho}_q = -\bar{\psi} \quad (3.30b)$$

$$\nabla \cdot \bar{\mathbf{v}} = 0 \quad (3.30c)$$

$$\frac{\partial(\bar{\rho}\bar{\mathbf{v}})}{\partial \bar{t}} + \nabla \cdot (\bar{\rho}\bar{\mathbf{v}}\bar{\mathbf{v}}) = -\nabla \bar{p} + \mathbf{G}\bar{\rho}_q + \frac{1}{\text{Re}}\bar{\mu}\nabla^2 \bar{\mathbf{v}} \quad (3.30d)$$

The boundary conditions for the velocities and electric potential are
Inlet ($\bar{x} = 0$)

$$\text{Velocities: } \bar{u} = \begin{cases} \bar{u}_{1,\text{in}} & \bar{y} \leq \delta_{\text{in}} \\ \bar{u}_{2,\text{in}} & \bar{y} > \delta_{\text{in}} \end{cases} \quad (5.50a)$$

$$\text{Electric potential: } \partial \bar{\psi} / \partial \bar{x} = 0 \quad (5.50b)$$

Outlet ($\bar{x} = L/H$)

$$\text{Velocities: } \partial \bar{u} / \partial \bar{x} = 0, \quad \partial \bar{v} / \partial \bar{x} = 0 \quad (5.50c)$$

$$\text{Electric potential: } \partial \bar{\psi} / \partial \bar{x} = 0 \quad (5.50d)$$

Wall ($\bar{y} = 0$)

$$\text{Velocities: } \bar{u} = 0, \bar{v} = 0 \quad (5.50e)$$

$$\text{Electric potential: } \bar{\psi} = \bar{\zeta}_w \quad (5.50f)$$

Wall ($\bar{y} = 1$)

$$\text{Velocities: } \bar{u} = 0, \bar{v} = 0 \quad (5.50g)$$

Interface ($\phi = 0$)

$$\text{Electric potential: } \bar{\psi} = \bar{\zeta}_s \quad (5.50h)$$

Where u is the velocity in x direction and v is the velocity in y direction. ζ_w is the zeta potential at the wall contacting with the aqueous solution. The wall in contact with the non-aqueous liquid does not acquire charges. ζ_s is the interfacial zeta potential between two liquids. Therefore, we do not specify the boundary condition of electric potential ψ at the wall ($y = h$). Instead, we specify the condition of at the interface (level set function $\phi = 0$). It is assumed two uniform velocities at the inlet for two liquids. $u_{1,\text{in}}$ is the inlet velocity for the aqueous solution and $u_{2,\text{in}}$ for the non-aqueous liquid. The interface position of the interface, δ_{in} , is prescribed if Y-shape microchannel used.

5.6.2 Validation of the Numerical Scheme

The numerical model presented in section 5.1 is validated by comparing the results with those from the exact solution of Chapter 4. Because the numerical model is two-dimensional, only two-liquid electroosmotic flows in two parallel plates is considered. To compare with the analytical solution, we set the width of the channel, w , of the analytical analysis to a very large value as compare to the height of the channel, h , say $w/h = 10^4$, therefore, the side wall effects can be neglected. The flow velocity and the symmetric line, where $z = 0$, can be treated as the flow velocity between two infinite parallel flat plates.

Unless otherwise specified, the aqueous solution is called liquid 1; while the non-

aqueous liquid is called liquid 2. The aqueous solution is also used to calculate reference values for non-dimensionalization purposes. As seen in Fig. 1.1, the two-liquid flow between two parallel plates of length L separated by a distance H . The height of liquid 1 is the entrance of the channel, δ_{in} . When an external electric field, E_x , is applied along the channel, the electroosmotic body force due to the presence of EDL causes the aqueous solution to flow. The aqueous solution drags the non-aqueous liquid along. The interface between two liquids evolves along the flow direction. The velocity profile and the interface position at every section change with the strength of the applied electric field, ions properties in the conducting fluid and the zeta potential at the wall in contact with the aqueous solution. Once fully developed, the velocity profile and the interface location become independent of the streamwise coordinate.

In modeling EO flow in microchannels, it is important that the EDL is captured accurately. The thickness of the EDL, $1/\kappa$, termed as Debye length, is in the order of 10nm-1 μ m. The region of varying potential extends to a distance of about $3\kappa D$ before the potential has decayed to about 2% of its value at the surface. On the other hand, the microchannels utilized in many lab-on-a-chip applications are between 1 μ m and 100 μ m. As a result, K is a big number and the electroosmotic forces are concentrated within a very thin region adjacent to a surface. Finer meshes near these affected regions are needed to capture the EDL forces accurately. In this section, successive meshes are used as shown in Fig. 5.10. The thickness of aqueous solution is set 0.3. We divided the whole domain into three regions. The height of the first one and second one is 0.26 each. As shown in Fig. 5.10, the successive ratio is defined as $r = l_i/l_{i-1}$, where l_i is the length of the i th grid. In the first region, the successive ratio $r = 1.5$ and $r = 0.67$ in the second region. The third region has uniform mesh. The final meshes are shown in Fig. 5.11 when the total number of mesh $n = 40$.

In the simulations, we fix the channel geometry $H = 100\mu\text{m}$ and $L = 150\mu\text{m}$. The externally applied electric field $E_x = 5000\text{v/m}$. The reference quantities μ_{ref} and ρ_{ref} are 10^{-3} Pa.s and 10^{-3} kg.m³, respectively. At these conditions, the velocity scale is

Figure 5.11: Schematic of mesh used in simulation.

$9 \times 10^{-5} \text{ m/s}$. The Reynolds number is about 9×10^{-3} and the Capillary number $\text{Ca} = 10$.

For a set of given viscosity ratio (β), applied electric field, pressure gradient, the fully developed thickness of the aqueous solution δ_{out}/H , depends on the volumetric flowrate ratio (q_2/q_1) of the two liquids. For this verification, liquid 1 occupies 30% of the channel at the inlet and the volumetric flowrate ratio is fixed such that both liquids occupy half of the channel in the fully developed region. The values of other parameters in this case are chosen as: $K = 20$, $\bar{\zeta}_w = 0.2$ and $\bar{\zeta}_s = 0.02$, $\bar{q}_1 = 6.60 \times 10^{-2}$ and $\bar{q}_2 = 2.23 \times 10^{-2}$. Fig. 5.12 shows the interface and the velocity profiles at five streamwise locations when $n = 120$ and $\beta = 1$.

Figure 5.12: Evolution of velocity and interface profiles along x/H and $\beta = 1$.

At the outlet, in Fig. 5.12, a comparison is shown to the exact velocity profile from the analytical solution presented in Chapter 5. Fig. 5.13 shows the detail comparisons of the fully developed velocity profiles obtained using various computational grids with the exact solution when $K = 20$. The results presented in Fig. 5.13 show the decay of discretization error with increased the total grid number n . It can be seen that the exact solution is reproduced accurately.

Figure 5.14 shows the comparisons of the fully developed velocity profiles obtained using four values of n with the exact solution when $K = 100$. A higher value of K results a thinner EDL. More grids are required to achieve the analytical solution.

Figure 5.13: Velocity profiles for various meshes when $K = 20$.

Figure 5.14: Velocity profiles for various meshes when $K = 100$.

From all of above results, we can conclude that the interface evolution between two fluids is well captured and this numerical method is suitable. In the following simulations, that $n = 120$ is used.

5.6.3 Two-liquid EOF Corresponding to Various Applied Electric Fields

In this section, the interfaces developments of two liquids due to various applied electric fields namely, favorably applied electric field and adversely applied electric field are examined. The focus of this problem is on the prediction of the interface evolution in the present of various external electric fields.

For a set of given viscosity ratio (β), volumetric flowrate ratio and pressure gradient, the fully developed thickness of the conducting fluid δ_{out}/H , varies with the applied electric field. The values of parameters in this case are chosen as: $K = 100$, $\bar{\zeta}_w = 4$, $\bar{\zeta}_s = 0.4$, and same volumetric flowrate $\bar{q}_2/\bar{q}_1 = 2$.

Figs. 5.15 and 5.16 show the evolutions of the interface and velocity profiles at the outlet for three different applied electric fields - no applied electric field, favorably and adversely applied electric fields, respectively. The favorable electric field is applied as $E = 5000\text{v/m}$, while the adverse one is applied as $E = -10000\text{v/m}$. Under favorably applied electric field, the electroosmotic forces will drag the aqueous solution to facilitate its flow in the same direction of the pressure gradient. But adversely applied electric field will generate an opposite electroosmotic force and work against the pressure-driven flow.

For the pure pressure driven flow, the two liquids occupy half of the channel at the fully developed region (outlet) due to the same viscosity. As the electroosmotic force is concentrated in the EDL region close to the wall contacting with the aqueous solution, the aqueous solution will flow faster in this region when a favorable electric field is applied. The average velocity of the aqueous solution becomes faster. As the results,

for the favorably applied electric field, the interface location at outlet becomes lower than the pure pressure driven flow. On the contrary, for the adversely applied electric fields, the aqueous solution will bear an electroosmotic force against the flow direction. Apparently the aqueous solution becomes more 'viscous' due to the adversely applied electric field. Therefore the aqueous solution will occupy more portion of the channel than the pure pressure driven flow as shown in Figs. 5.15 and 5.16.

Figure 5.15: The interface profiles along x/H for $\beta = 1$ and $\zeta_s = 0.1\zeta_w$.

Figures 5.17 and 5.18 show the evolutions of the interface and velocity profiles at the outlet for the three different applied electric fields when the viscosity ratio $\beta = 5$. Since the non-aqueous liquid is more viscous, to achieve the same volumetric flowrates, the more viscous fluid has to spread to a large portion. The results further indicate that by adjusting the magnitude and direction of electric field, electroosmosis effect can be used to control the interface location of a pressure driven flow in microfluidics channels.

The velocities of two liquids can be considered as a linear combination of the electroosmotic flow and a pressure driven flow. In the cases of adversely applied electric field, the electroosmotic flow works against the pressure driven flow. Depending on the magnitude of the electric fields, reverse flow occurs when the electroosmotic force is

Figure 5.16: The velocity profiles at outlet for $\beta = 1$ and $\zeta_s = 0.1\zeta_w$.

strong enough as shown in Figs. 5.16 and 5.18.

Figure 5.19 shows the interface and the velocity profiles at five streamwise locations for various applied electric field when $\beta = 5$. It can be seen that the present procedure captures the interface location and resolve the EDL correctly.

Figure 5.17: The interface profiles along x/H for $\beta = 5$ and $\zeta_s = 0.1\zeta_w$.

Figure 5.18: The velocity profiles along outlet for $\beta = 5$ and $\zeta_s = 0.1\zeta_w$.

(a) No applied electric field

(b) Favorably applied electric field

(c) Adversely applied electric field

Figure 5.19: Evolutions of velocity and interface profiles along x/H when $\beta = 5$ and $\zeta_s = 0.1\zeta_w$.

Chapter 6

Conclusions and Future Studies

In this chapter, a summary of the major accomplishments and findings arising out of the investigation in this dissertation is given and future work studies are presented.

6.1 Summary of Investigations

Following the objectives of this thesis, extensive and rigorous modeling on the two-liquid stratified electroosmotic flow in rectangular microchannel has been developed. The proposed models are solved using analytical and numerical methods. The major contributions made during the course of this study can be summarized as follows:

Interfacial conservation equation

The governing equations for interfacial conservation are obtained by considering the control volume including the interface. Jump conditions through the interface are derived. The presence of surface charges at the interface induces a jump of pressure in normal direction and jump of stresses in tangential direction of the interface. This work provides a rigorous mathematical foundation for future studies.

Two-liquid stratified electroosmotic flow

Steady and transient two-liquid stratified electroosmotic flows in rectangular microchannels are solved analytically using the separation of variables method. In modeling of the charge distributions in the electric double layer (EDL), the Boltzmann distribution is assumed, from which the Poisson-Boltzmann equation is obtained. The surface charge density is obtained analytically from the gradient of the electric potential.

The analytical solutions of two-liquid flow driven by electroosmosis and pressure gradient are obtained. The flow characteristics depend on the coupling effect between the two liquids. The coupling condition involves the opposite electrostatic force exerted on the interface and the hydrodynamic shear stress between the two liquids. The effects of viscosity ratio, interfacial zeta potential, EDL parameter and channel aspect ratio are discussed. When the viscosity ratio is higher, the flow resistance of the non-aqueous solution liquid is higher, resulting in a steeper velocity gradient at the interface of the aqueous solution. For an extreme case, the infinite viscosity of the non-aqueous solution liquid makes the flow of the non-aqueous solution liquid resemble to that of the channel wall. Comparison is made between the present exact velocity profile and the exact solution of single liquid when the viscosity of non-aqueous solution liquid is very large. Interfacial zeta potential is also an important parameter that affects the velocity profile.

The dynamic aspects of the two-liquid electroosmotic flow are studied by solving the transient governing equations using the Laplace transform method. The time evolution of the velocity field of the two liquids is obtained. It is found that during the initial transient time, the non-aqueous solution liquid moves in the opposite direction. As time elapses, negative velocity reduces as the EDLs exert a hydrodynamic shear stress on its adjacent liquid.

A method to control interface position between two liquids by electroosmosis

An novel method to control the interface position between two liquids by electroosmosis is experimentally studied. Two fluids, aqueous NaCl solution and aqueous glycerol were introduced by syringe pumps to flow side by side in a straight microchannel. An external electric field was applied on the NaCl side. Under the same inlet volumetric flowrates condition, the results show that the interface location can be controlled by adjusting the direction and strength of the applied electric field.. The interface position between the two fluids with the electroosmosis effect was studied using fluorescence imaging technique. The velocity field was measured using micro-PIV technique. The parameters, flowrate and electric field, which affect the interface position and velocity field were investigated. The measured velocity field agrees well with that of theoretical analysis.

A novel numerical scheme for jump conditions

The presences of surface tension and surface charges result in the jump in pressure and stress across the interface between two liquids. Finite difference method is used to deal with these jump conditions. One dimensional Poisson equation is considered first. The jump of variables and its gradients are considered as body forces in the final discretization equation. Unlike the continuous stress method, this method does not smear the solution because it captures the jump condition exactly in one grid. This method can also be easily to expand to two dimensional or three dimensional problems. One dimensional and two dimensional heat conduction problems are considered to verify the scheme. The results obtained by the proposed numerical scheme agree with the corresponding analytical solutions.

The jump conditions are expressed in the forms suitable for numerical simulation to be integrated in the SIMPLER algorithm.

6.2 Future Work

Having performed the above investigations, it is recommended that additional work needs to be carried out to achieve more comprehensive understanding of the two-liquid electroosmotic flow in microchannels.

Suggested future studies are as follows:

1. Flow metering and switching

When there are two or more different fluids co-flowing in the microchannel, distinguishable interfaces between the fluids can be expected because no turbulence occurs and the molecular diffusion between the fluid streams is negligibly small. This laminar flow provides the possibility of flow handling such as accurate flow metering and switching. The present model can be extended to microfluidic flow switches design. The flow switching can be achieved by controlling the flow rate ratios and the electroosmotic force at the interface.

2. Two-phase flow pattern in microchannels

Two-phase flow in a microchannel is different from that in a macrochannel. Surface effects dominate in small devices. The surface-to-volume ratio for a MEMS device having a size of $10\mu\text{m}$ is 10^5m^{-1} . The million-fold increase in surface area relative to the mass of microchannel affects the transport of mass, momentum and energy through the surface. Therefore, two-phase flow patterns in microchannels are different from those encountered in ordinarily sized tubes. It has been confirmed that two-phase flow pattern are sensitive to the entrance conditions and the surface conditions of the inner wall of the test tubes. To study the two-phase flow in the microchannel, experiments are suggested to be conducted.

3. 3D numerical simulation

Until now, our program is only used for two dimensional problems. A three dimensional program should be developed for simulation of more complex problems.

In this thesis, only the two-liquid stratified electroosmotic flow is investigated. Other flow pattern such as droplet flow should be investigated. Then, the three dimensional program will be very useful.

Publications resulting from this thesis

Refereed Journals:

1. **Yandong Gao**, Cheng Wang, Teck Neng Wong, Chun Yang and Kim Tiow Ooi, Electroosmotic control of the interface position of two-liquid flow through a microchannel, *Journal of Micromechanics and Microengineering*, accepted, 2006
2. Cheng Wang, **Yandong Gao**, Nam-Trung Nguyen, Teck Neng Wong, Chun Yang and Kim Tiow Ooi, Interface control of pressure-driven two-fluid flow in microchannels using electroosmosis, *Journal of Micromechanics and Microengineering*, 15:2289-2297, 2005
3. **Yandong Gao**, Teck Neng Wong, John C.Chai, Chun Yang and K.T. Ooi, Numerical simulation of two-fluid electroosmotic flow in microchannels, *International Journal of Heat and Mass Transfer*, 266:117-128, 2005
4. **Yandong Gao**, Teck Neng Wong, Chun Yang and Kim Tiow Ooi, Transient Two-liquid Electroosmotic Flow with Electric Charges at the Interface, *Colloids and Surfaces, A: Physiochem. and Eng. Asp.*, 266: 117C128, 2005
5. **Yandong Gao**, Teck Neng Wong, Chun Yang and Kim Tiow Ooi, Two-fluid electroosmotic flow in microchannels, *Journal of Colloid and Interface Science*, 284:306-314, 2005

Conference Papers:

1. **Yandong Gao**, Y.F. Yap, T.N. Wong, J.C.Chai, , C.Yang and K.T. Ooi, Numerical solution of two-fluid electroosmotic flow, Proceedings of ICMM2005, 3rd International Conference on Microchannels and Minichannels June 13-15, 2005, Toronto, Ontario, Canada
2. **Gao Yandong**, Wang Cheng, Wong T.N., Yang C, Nguyen NT and Ooi K.T, Electroosmotic control of the interface between two-liquid flowing through a microchannel, Proceedings of Symposium F, ICMAT2005 & ICAM 2005, 3rd International Conference on Materials for Advanced Technologies and 9th International Conference on Advanced Materials. 3-8 July, 2005, Singapore

Appendix A

Transport Balance Laws for Interface

A.1 Intrinsic definition of interface

Consider a system of two immiscible fluids (fluid I and fluid II), the fluids are separated by a moving interfacial region. It is convenient to use orthogonal curvilinear coordinates as shown in Fig. A.1. In most cases the surfaces in the interfacial region are assumed to be parallel structure. A coordinate surface $S(x_3, t)$ is identical as a surface, which is obtained for a given value of one curvilinear coordinate, x_3 . For example, the S surface is corresponding to $x_3 = 0$. The boundaries of the interfacial regions are obtained by the values of x_I and x_{II} , corresponding to the surfaces S_I and S_{II} as shown in Fig. A.1. The intrinsic definition of the surface is

$$F(\mathbf{r}, t) = 0 \quad (3.1)$$

By this description of interface, only the normal velocity of the surface is well defined,

which is corresponding to the movement of the geometrical surface,

$$w_{\perp}^s = -\frac{\partial F / \partial t}{|\nabla F|} \quad (\text{A.1})$$

This velocity corresponds to the movement of the geometric surface. Other (tangential) velocity at the surface cannot be well defined by this description of interface. In most situations, the interfacial velocity, $\mathbf{w}^s$, is defined as a composite velocity, consisting the above normal geometrical velocity, $w_{\perp}^s$ and tangential component of the local material velocity $\mathbf{v}$

$$\mathbf{w}^s = (\mathbf{I} - \mathbf{nn}) \cdot \mathbf{v} + \mathbf{n}w_{\perp}^s \quad (\text{A.2})$$

where $\mathbf{n}$ is the unit normal vector and $\mathbf{I}$ is the second order identity tensor.

A.2 Interfacial Conservation Equation

Boundary conditions or coupling conditions should be defined properly at the interface. There are two approaches to describe the interface. The first one is to regard the interface separating two immiscible fluids as a geometrical surface. Jump conditions through the interface are derived from the conservation equations [Bedeaux et al., 1976; Kovac, 1977; Scriven, 1960; Slattey, 1990]. The second approach is to consider a thin transition layer called the interfacial layer between two fluids. Because the thickness of the interfacial layer is small compared to the radius of the mean curvature of the macroscopic surface replacing the layer, the interfacial layer is replaced by a discontinuous surface (interface) where interface quantities are defined by integration over the thickness of the layer [Gatignol and Prud'homme, 2001; Ishii, 1975]. To provide a better understanding of the derivation of the interfacial conservation equations, the second approach is used here. In the following, the integral form of the conservation is used to establish conservation equations at interface.

A.2.1 General conservation equation at a discontinuous interface

This section develops equations that describe the dynamics of Newtonian fluids that contain a discontinuous interface. Consider a cylindrical control volume $\mathcal{V}$ shown in Fig. A.1, which encloses part of the interface, S between fluids I and fluid II . The cylindrical control volume is bounded by portion of S_I surface, $\partial\mathcal{V}_I$, portion of S_{II} surface, $\partial\mathcal{V}_{II}$ and a lateral surface $\partial\mathcal{V}_{lat}$.

The cylindrical control volume is constructed so that its edges are normal to the interface of area A , bounded by curve L . The normal unit vector to S is denoted by $\mathbf{n}$ and the tangential unit vector to L is $\boldsymbol{\tau}$. Another unit vector $\boldsymbol{\xi}$, normal to the lateral surface $(\partial\mathcal{V})_{lat}$, is defined as $\boldsymbol{\xi} = \boldsymbol{\tau} \times \mathbf{n}$. The height of the cylindrical control volume is small compared with the radius of the curvature of the interface.

Figure A.1: Curvilinear orthogonal coordinates and the control volume containing the interfacial layer

Interface quantities are obtained by integration of bulk quantities through the interfacial domain. The interface mass density ρ^s (mass per unit interfacial area) is defined as

$$\rho^s = \int_{x_{3I}}^{x_{3II}} \rho \, dx_3 \quad (\text{A.3})$$

where ρ is the mass per unit volume. One can define any quantity θ^s at the interface as

$$\rho^s \theta^s = \int_{x_{3I}}^{x_{3II}} \rho \theta \, dx_3 \quad (\text{A.4})$$

Applied to the momentum, this gives a definition of the mean surface velocity of the fluid on the interface,

$$\rho^s \mathbf{w}^s = \int_{x_{3I}}^{x_{3II}} \rho \mathbf{w} \, dx_3 \quad (\text{A.5})$$

where $\mathbf{w}^s$ is the mean surface velocity.

The integral form of conservation equation for any quantity, θ , is

$$\frac{d_{\mathbf{w}^s}}{dt} \int_{\mathcal{V}} \rho \theta \, d\mathcal{V} + \int_{\partial\mathcal{V}} [\mathbf{J} + \rho \theta (\mathbf{v} - \mathbf{w}^s)] \cdot \mathbf{n} \, dS = \int_{\mathcal{V}} \rho \dot{\theta} \, d\mathcal{V} \quad (\text{A.6})$$

where $\mathbf{v}$ is the velocity of the continuum, $\mathbf{J}$ is the transport flux, $\mathbf{n}$ is the outward unit normal to $\partial\mathcal{V}$, $\rho \dot{\theta}$ is the volumetric production of the property and $\frac{d_{\mathbf{w}^s}}{dt} = \frac{\partial}{\partial t} + \mathbf{w}^s \cdot \nabla$ is the material time derivative at the surface.

As the interfacial layers are parallel. The normal unit vectors to surface S , S_I and S_{II} are same. Applying the conservation equation (A.6) to the this cylindrical control volume of $\mathcal{V}$ yields

$$\begin{aligned} \frac{d_{\mathbf{w}^s}}{dt} \int_{\mathcal{V}} \rho \theta \, d\mathcal{V} + \int_{\partial\mathcal{V}_I} [\mathbf{J} + \rho \theta (\mathbf{v} - \mathbf{w}^s)] \cdot \mathbf{n} \, dS + \int_{\partial\mathcal{V}_{II}} [\mathbf{J} + \rho \theta (\mathbf{v} - \mathbf{w}^s)] \cdot \mathbf{n} \, dS \\ + \int_{(\partial\mathcal{V})_{\text{lat}}} [\mathbf{J} + \rho \theta (\mathbf{v} - \mathbf{w}^s)] \cdot \boldsymbol{\xi} \, dS = \int_{\mathcal{V}} \rho \dot{\theta} \, d\mathcal{V} \end{aligned} \quad (\text{A.7})$$

Here the boundary of this control volume $\partial\mathcal{V}$ has been written into three parts: $\partial\mathcal{V}_I$, $\partial\mathcal{V}_{II}$ and $(\partial\mathcal{V})_{\text{lat}}$.

As the thickness of the interfacial layer, $(x_I - x_{II})$, is much smaller compared with the mean curvature of S , which is $\kappa = -\nabla \cdot \mathbf{n}$, the following approximations are obtained:

$$\int_{\mathcal{V}} \rho \theta \approx \int_{\mathcal{A}} \left(\int_{x_{3I}}^{x_{3II}} \rho \theta \, dx_3 \right) d\mathcal{A} = \int_{\mathcal{A}} \rho^s \theta^s \, d\mathcal{A}$$

$$\begin{aligned}
 \int_{(\partial\mathcal{V})_{\text{lat}}} [\mathbf{J} + \rho\theta(\mathbf{v} - \mathbf{w}^s)] \cdot \boldsymbol{\xi} \, dS &\approx \int_L \left(\int_{x_{3I}}^{x_{3II}} [\mathbf{J} + \rho\theta(\mathbf{v} - \mathbf{w}^s)] \, dx_3 \right) \cdot \boldsymbol{\xi} \, dL \\
 \int_{\partial\mathcal{V}_I} [\mathbf{J} + \rho\theta(\mathbf{v} - \mathbf{w}^s)] \cdot \mathbf{n} \, dS &\approx - \int_{\mathcal{A}} [\mathbf{J} + \rho\theta(\mathbf{v} - \mathbf{w}^s)]_I \cdot \mathbf{n} \, dA \\
 \int_{\partial\mathcal{V}_{II}} [\mathbf{J} + \rho\theta(\mathbf{v} - \mathbf{w}^s)] \cdot \mathbf{n} \, dS &\approx + \int_{\mathcal{A}} [\mathbf{J} + \rho\theta(\mathbf{v} - \mathbf{w}^s)]_{II} \cdot \mathbf{n} \, dA \\
 \int_{\mathcal{V}} \rho\theta &\approx \int_{\mathcal{A}} \left(\int_{x_{3I}}^{x_{3II}} \rho\dot{\theta} \, dx_3 \right) dA = \int_{\mathcal{A}} \rho_a \dot{\theta}^s \, dA \quad (\text{A.8})
 \end{aligned}$$

Substituting the above approximations into the Eq. (A.7) yields

$$\begin{aligned}
 \frac{d\mathbf{w}^s}{dt} \int_{\mathcal{A}} \rho_a \theta^s \, dA + \int_{\mathcal{A}} [[\mathbf{J} + \rho\theta(\mathbf{v} - \mathbf{w}^s)]] \cdot \mathbf{n} \, dA \\
 + \int_L \left\{ \int_{x_{3I}}^{x_{3II}} [\mathbf{J} + \rho\theta(\mathbf{v} - \mathbf{w}^s)] \, dx_3 \right\} \cdot \boldsymbol{\xi} \, dL = \int_{\mathcal{A}} \rho_a \dot{\theta}^s \, dA \quad (\text{A.9})
 \end{aligned}$$

where the notation $[[\phi]] = \phi_{II} - \phi_I$ is the jump quantity between the two values of ϕ taken respectively on the boundaries of the interfacial layer. The interfacial transport flux can be defined as

$$\mathbf{J}^s = \int_{x_{3I}}^{x_{3II}} [\mathbf{J} + \rho\theta(\mathbf{v} - \mathbf{w}^s)] \, dx_3 \quad (\text{A.10})$$

Finally, the integral form of the conservation equation is written as

$$\frac{d\mathbf{w}^s}{dt} \int_{\mathcal{A}} \rho^s \theta^s \, dA + \int_{\mathcal{A}} [[\mathbf{J} + \rho\theta(\mathbf{v} - \mathbf{w}^s)]] \cdot \mathbf{n} \, dA + \int_L \mathbf{J}^s \cdot \boldsymbol{\xi} \, dL = \int_{\mathcal{V}} \rho^s \dot{\theta}^s \, d\mathcal{V} \quad (\text{A.11})$$

The surface divergence theorem and the surface transport theorem [Gatignol and Prud'homme, 2001, chp. 2] can be written as

$$\begin{aligned}
 \int_L \mathbf{J}^s \cdot \boldsymbol{\xi} \, dL &= \int_{\mathcal{A}} \nabla_s \cdot [(\mathbf{I} - \mathbf{nn}) \cdot \mathbf{J}^s] \, dA \\
 \frac{d\mathbf{w}^s}{dt} \int_{\mathcal{A}} \rho_a \theta_s \, dA &= \int_{\mathcal{A}} \left(\frac{d\mathbf{w}^s}{dt} \rho_a \theta_s + \rho_a \theta_s \nabla_s \cdot \mathbf{w}^s \right) dA \quad (\text{A.12})
 \end{aligned}$$

where the notation $(\mathbf{I} - \mathbf{nn})$ is the tangential projection operation, which projects any

vector onto the tangential direction. The notation $\nabla_{||} = (\mathbf{I} - \mathbf{nn}) \cdot \nabla$ is the tangential gradient operator. Using Eqs. (A.10) and (A.12), Eq. (A.9) becomes

$$\frac{d_{\mathbf{w}^s}(\rho_a \theta^s)}{dt} + (\rho_a \theta^s) \nabla_s \cdot \mathbf{w}^s + \llbracket \mathbf{J} + \rho \theta (\mathbf{v} - \mathbf{w}^s) \rrbracket \cdot \mathbf{n} + \nabla_s \cdot \mathbf{J}_{||}^s = \rho_a \dot{\theta}_s \quad (\text{A.13})$$

where $\mathbf{J}_{||}^s = (\mathbf{I} - \mathbf{nn}) \cdot \mathbf{J}^s$. Eq. A.13 is the differential form of the general conservation equations for interface.

A.2.2 Interfacial mass balance

The result of Eq. (A.13) is applied first to total mass. There is no diffusive flux for total mass, it can be deduced that $\theta = \theta^s = 1$ and $\mathbf{J} = 0$. There is no sources or sinks of mass $\dot{\theta}_s = 0$. In addition, there is no net mass flow relative to the mean surface velocity at the interface,

$$\begin{cases} \rho^s \theta_s = \rho^s = \int_{x_{3I}}^{x_{3II}} \rho dx_3 \\ \mathbf{J}^s = \int_{x_{3I}}^{x_{3II}} \rho (\mathbf{v} - \mathbf{v}^s) d\xi = \int_{\xi_I}^{\xi_{II}} \rho \mathbf{v} dx_3 - \int_{\xi_I}^{\xi_{II}} \rho \mathbf{v}^s dx_3 \end{cases} \quad (\text{A.14})$$

Thus Eq. (A.13) becomes

$$\frac{\partial \rho^s}{\partial t} + \nabla_s \cdot (\rho^s \mathbf{w}^s) + \llbracket \rho (v_{\perp} - w_{\perp}^s) \rrbracket \cdot \mathbf{n} = 0 \quad (\text{A.15})$$

As usual, this equation can be written in a condensed form: $\dot{m}_a + \llbracket \dot{m} \rrbracket = 0$, where $\dot{m}$ is the quantity: $\dot{m} = \rho (\mathbf{v} - \mathbf{w}_s) \cdot \mathbf{n} = \rho (v_{\perp} - w_{\perp}^s)$, that is

$$\llbracket \dot{m} \rrbracket = \llbracket \rho (\mathbf{v} - \mathbf{w}^s) \cdot \mathbf{n} \rrbracket \quad (\text{A.16})$$

Using this balance law for the mass, the general surface balance law (A.13) for interface becomes

$$\rho_a \frac{d_{\mathbf{w}_s} \theta_s}{dt} + \llbracket J_{\perp} + \dot{m} (\theta - \theta_s) \rrbracket + \nabla_s \cdot \mathbf{J}_{a||} = \rho_a \dot{\theta}_s \quad (\text{A.17})$$

A.2.3 Stress balance with surface tension at an interface

Equation (A.17) is applied to momentum balance at an interface. The general momentum balance must still hold. We have: $\theta = \mathbf{v}$, $\theta^s = \mathbf{v}^s$, $\mathbf{J} = -\mathbf{T}$, $\mathbf{J}^s = -\mathbf{T}^s$ and $\dot{\theta}^s = \mathbf{f}^s$. Substituting them into Eq. (A.17) yields

$$\rho_a \frac{d_s \mathbf{v}_s}{dt} + [[\dot{m}(\mathbf{v} - \mathbf{v}_s) - \mathbf{T} \cdot \mathbf{n}]] - \nabla_s \cdot [(\mathbf{I} - \mathbf{nn}) \cdot \mathbf{T}^s] = \rho_a \mathbf{f}_s \quad (\text{A.18})$$

It is defined that $(\mathbf{I} - \mathbf{nn}) \cdot \mathbf{T}^s = \mathbf{T}_{||}^s$, which is called interface stress tensor. For simple liquid, the interface stress tensor is

$$\mathbf{T}_{||}^s = \sigma(\mathbf{I} - \mathbf{nn}) \quad (\text{A.19})$$

where σ is the surface tension.

Here we consider a simple situation, capillary surface without mass, $\rho^s = 0$ and $\mathbf{f}^s = 0$. Moreover, there is no mass flow rate through the capillary surface ($\dot{m} = 0$). Then Eq. (A.18) reduces to

$$[[\mathbf{T} \cdot \mathbf{n}]] + \nabla_s \cdot [\sigma(\mathbf{I} - \mathbf{nn})] = 0 \quad (\text{A.20})$$

The pressure stress tensor, defined in Eq. (3.6) is rewritten as

$$\mathbf{T} = -p\mathbf{I} + \mathbf{T}' \quad (\text{A.21})$$

where $\mathbf{T}' = \mu(\nabla \mathbf{v} + \nabla \mathbf{v}^T) + (\lambda \nabla \cdot \mathbf{v})\mathbf{I}$ is the viscosity stress tensor. Then Eq. (A.20) is rewritten as

$$-[[\mathbf{T}' \cdot \mathbf{n}]] + [[p]]\mathbf{n} - \nabla_s \cdot (\sigma \mathbf{I}_{||}) = 0 \quad (\text{A.22})$$

One also has

$$\nabla_s \cdot (\sigma \mathbf{I}_{||}) = \nabla_s \sigma - \sigma(\nabla \cdot \mathbf{n})\mathbf{n} \quad (\text{A.23})$$

Therefore, the desired stress balance at any point on an interface is obtained

$$- [[\mathbf{T}' \cdot \mathbf{n}]] + [[p]] \mathbf{n} - \nabla_s \sigma + \sigma (\nabla \cdot \mathbf{n}) \mathbf{n} = 0 \quad (\text{A.24})$$

By projection of Eq. (A.24) into the normal direction $\mathbf{n}$, the normal stress balance at interface

$$[[p]] = -\sigma \nabla \cdot \mathbf{n} + [[T']] : \mathbf{nn} = \kappa \sigma + [[T']] : \mathbf{nn} \quad (\text{A.25})$$

where $\kappa = -\nabla \cdot \mathbf{n}$. The result indicates that jump in normal stress across the interface must balance the curvature force per unit area. Projection Eq. (A.24) into the tangential direction yields the tangential stress balance at the interface

$$\nabla_s \sigma + \mathbf{n} \cdot [[\mathbf{T}']] \cdot (\mathbf{I} - \mathbf{nn}) = 0 \quad (\text{A.26})$$

Here the surface tension, σ , may vary along the surface S under the effects of nonhomogeneous temperature or concentrations. The tangential gradient of surface tension, $\nabla_s \sigma$, causes the fluids to flow along the interface. This phenomenon is called the Bénard-Marangoni effect.

Appendix B

Numerical Inversion of the Laplace Transforms

For Laplace transform, simple functions can be treated with transform tables. Software packages, such as MathCAD, MAPLE and MATHEMATICA, allow the user to obtain the analytical transform and inverse. However complicated transform functions(e.g. Eqs. (4.31a) and (4.31c) arise which are tedious to invert by the analytical methods. So, the numerical inversion of Laplace transform functions is sometimes necessary to obtain an approximate solution.

The Laplace transform of a real-valued function $f(\tau)$, is given by the following integral where s is a complex quantity $s = \sigma + j\omega$ known as the Laplace variable.

$$F(s) = \int_0^{\infty} e^{-s\tau} f(\tau) d\tau \quad (\text{B.1})$$

There are two restrictions on $f(\tau)$ that are necessary for the integral to exit:

- $f(\tau)$ must be piecewise continuous;
- $f(\tau)$ must be exponential order: $|f(\tau)| < Me^{\sigma\tau}$

The inverse transform $f(\tau)$ is defined by the inversion formula

$$f(\tau) = \frac{1}{2j\pi} \int_{\sigma-j\omega}^{\sigma+j\omega} e^{s\tau} F(s) ds \quad (\text{B.2})$$

A wide variety of numerical methods exists to calculate such integral. Only one complementary method - Gaver-Stehfest Method.- will be presented here.

The Gaver-Stehfest algorithm is a slightly modified version of the Stehfest method, also called BigNumber-Stehfest method. This inversion technique has been proposed by Stehfest and the inversion equation can be written in the following way:

$$f(\tau) \cong \frac{\ln(2)}{\tau} \sum_{j=1}^N V_j F\left(\frac{j \ln(2)}{\tau}\right) \quad (\text{B.3})$$

This corresponds to the optimized coefficients

$$a_j = j \ln(2) \quad (\text{B.4})$$

and

$$V_j = (-1)^{j+N/2} \sum_{k=\text{Int}((j+1)/2)}^{\text{Min}(N/2,j)} \frac{k^{N/2}(2k)!}{(N/2 - k)!k!(k-1)!(j-k)!(2k-j)!} \quad (\text{B.5})$$

N depends on the floating-point precision of the computer. With single precision, $N = 10$ is often the most suitable choice. Expression B.5 yields as shown in table B.1. With double precision, it is possible to use $N = 20$. It yields then as table B.2

This method can be implemented with a very simple algorithm, without adjustable parameters. However, it is not necessary to increase N , since the number of significant digits is fixed. This point limits the precision of the great numbers such as the factorials used in the calculation of the V_j coefficients.

Table B.1: Set of ten constants for V for the Gaver-Stehfest method

j	V_j
1	$+8.333333333333331e - 02$
2	$-3.208333333333333e + 01$
3	$+1.279000000000000e + 03$
4	$-1.562366666666667e + 04$
5	$+8.424416666666667e + 04$
6	$-2.369575000000000e + 05$
7	$+3.759116666666667e + 05$
8	$-3.400716666666667e + 05$
9	$1.640625000000000e + 05$
10	$-3.281250000000000e + 04$

Table B.2: Set of twenty constants for V for the Gaver-Stehfest method

j	V_j
1	$-5.511463844797178e - 06$
2	$+1.523864638447972e - 01$
3	$-1.174654761904762e + 02$
4	$+1.734244933862434e + 04$
5	$-9.228069289021164e + 05$
6	$+2.377408778710318e + 07$
7	$-3.494200661953704e + 08$
8	$+3.241369852231879e + 09$
9	$-2.027694830723779e + 10$
10	$+8.946482982379724e + 10$
11	$-2.870209211471027e + 11$
12	$+6.829920102815115e + 11$
13	$-1.219082330054374e + 12$
14	$+1.637573800842013e + 12$
15	$-1.647177486836117e + 12$
16	$+1.221924554444226e + 12$
17	$-6.488065588175326e + 11$
18	$+2.333166532137059e + 11$
19	$-5.091380070546738e + 10$
20	$+5.091380070546738e + 09$

Appendix C

Pressure and Stress Jump across the Interface

On the interface between two liquids, one has the jump conditions

$$[[p]] = 2 [[\mu]] (\nabla u \cdot \mathbf{n}, \nabla v \cdot \mathbf{n}) \cdot \mathbf{n} + \kappa \sigma + \rho_q^s \mathbf{E} \cdot \mathbf{n} \quad (5.7)$$

to the normal direction and

$$\begin{aligned} \begin{pmatrix} [[\mu u_x]] & [[\mu u_y]] \\ [[\mu v_x]] & [[\mu v_y]] \end{pmatrix} &= [[\mu]] \begin{pmatrix} \nabla u \\ \nabla v \end{pmatrix} \begin{pmatrix} \mathbf{0} \\ \mathbf{t} \end{pmatrix}^T \begin{pmatrix} \mathbf{0} \\ \mathbf{t} \end{pmatrix} + [[\mu]] \mathbf{n}^T \mathbf{n} \begin{pmatrix} \nabla u \\ \nabla v \end{pmatrix} \mathbf{n}^T \mathbf{n} \\ &\quad - [[\mu]] \begin{pmatrix} \mathbf{0} \\ \mathbf{t} \end{pmatrix}^T \begin{pmatrix} \mathbf{0} \\ \mathbf{t} \end{pmatrix} \begin{pmatrix} \nabla u \\ \nabla v \end{pmatrix}^T \mathbf{n}^T \mathbf{n} - \begin{pmatrix} \mathbf{n} \\ \mathbf{t} \end{pmatrix}^T \begin{pmatrix} 0 & 0 \\ \rho_q^s \mathbf{E} \cdot \mathbf{t} & 0 \end{pmatrix} \begin{pmatrix} \mathbf{n} \\ \mathbf{t} \end{pmatrix} \end{aligned} \quad (5.10)$$

to the tangential direction

Here we rewrite them in index notation. Eq. (5.7) can be written as

$$[[p]] = 2 [[\mu]] (n_1^2 u_x + n_1 n_2 (u_y + v_x) + n_2^2 v_y) + \kappa \sigma + \rho_q^s E_n \quad (C.1)$$

where $(n_1, n_2) = \mathbf{n}$ and E_n is the electric field in the normal direction.

Equation (5.10) is written by each terms

$$\begin{aligned} \llbracket \mu u_x \rrbracket = \llbracket \mu \rrbracket \left[(n_1^4 - n_1^2 t_1^2 + t_1^2) u_x + (n_1^3 n_2 - n_1^2 t_1 t_2 + t_1 t_2) u_y + \right. \\ \left. (n_1^3 n_2 - n_1 n_2 t_1^2) v_x + (n_1^2 n_2^2 - n_1 n_2 t_1 t_2) v_y \right] - t_1 n_1 \rho_q^s \llbracket E \rrbracket_+ \cdot \mathbf{t} \quad (\text{C.2a}) \end{aligned}$$

$$\begin{aligned} \llbracket \mu u_y \rrbracket = \llbracket \mu \rrbracket \left[(n_1^3 n_2 - n_1 n_2 t_1^2 + t_1 t_2) u_x + (n_1^2 n_2^2 - n_1 n_2 t_1 t_2 + t_2^2) u_y + \right. \\ \left. (n_2^3 n_1 - n_2^2 t_1 t_2) v_y \right] - t_1 n_2 \rho_q^s \llbracket E \rrbracket_+ \cdot \mathbf{t} \quad (\text{C.2b}) \end{aligned}$$

$$\begin{aligned} \llbracket \mu v_x \rrbracket = \llbracket \mu \rrbracket \left[(n_1^3 n_2 - n_1^2 t_1 t_2) u_x + (t_1^2 + n_1^2 n_2^2 - n_1 n_2 t_1 t_2) v_x + \right. \\ \left. (t_1 t_2 + n_1 n_2^3 - n_1 n_2 t_2^2) v_y \right] - t_2 n_1 \rho_q^s \llbracket E \rrbracket_+ \cdot \mathbf{t} \quad (\text{C.2c}) \end{aligned}$$

$$\begin{aligned} \llbracket \mu v_y \rrbracket = \llbracket \mu \rrbracket \left[(n_1^2 n_2^2 - n_1 n_2 t_1 t_2) u_x + (n_2^3 n_1 - n_1 n_2 t_2^2) u_y + \right. \\ \left. (t_1 t_2 + n_2^3 n_1 - n_2^2 t_1 t_2) v_x + (t_2^2 + n_1^4 - n_2^2 t_2^2) v_y \right] - t_1 n_1 \rho_q^s \llbracket E \rrbracket_+ \cdot \mathbf{t} \quad (\text{C.2d}) \end{aligned}$$

Appendix D

Verification of Numerical Scheme by Heat Conduction Problem

The scheme in this study is designed to perform a finite volume analysis for jump interface conditions. Verification, in general, consists of checking the scheme on a set of problems which test its various capabilities. Analytical solutions are, in principle, ideal for testing the accuracy of numerical methods. The problems of heat conduction with heat resistance are simulated using the scheme developed in Chapter 5. Here the verification of the scheme is performed by solve general Poisson equations, where the coefficients, variables and its flux may jump across an interface.

D.0.4 One dimension heat conduction in two homogeneous materials with heat generation

Figure D.1(a) shows a one-dimensional conduction through a plane composite material in contact at the interface $x_\Gamma = 0.5$. There is heat generation in the region 1 as $S = 40$. The left boundary is subjected to a constant heat flux $q_{in} = 10$. The temperature is set to zero at the right boundary. The thermal conductivities of the two material are $k_1 = 0.5$ and $k_2 = 1$, respectively. The contact resistance at the interface is set to $R_j = 0.5$. As

(a) represent of the problem

(b) temperature distributions with temperature jump (contact resistance) for different grids

Figure D.1: One dimensional heat conduction problem.

the analytical solution, the temperature in the region 1 is $T(x) = 40x^2 - 20x + 50$ and $T(x) = 15 - 30 * (x - 0.5)$ in the region 2. There is a sharp jump in the temperature at the interface due to the contact resistance. Fig. D.1(b) shows the comparison of results with different grid sizes. It can be seen that the exact solution is reproduced even with the relatively coarse meshes.

D.0.5 Two dimensional heat conduction in two homogenous materials with a rectangular inside

In the second problem, the computational domain is $[0, 10] \times [0, 10]$. The interior (region 1) has a rectangular shape, which has the corners in (1, 8), (2, 9), (8, 1) and (9, 2). The remainder of computational domain is the exterior region (region 2). The contact resistance between two regions is $R_j = 0.5$. The thermal conductivities of interior region is $k_1 = 1$ and one of exterior region is $k_2 = 1000$, respectively. Dirichlet's conditions, $T = 0$, are defined at the boundaries of the domain. There is heat generation in the interior domain one as $S = 20$. The grid size is 40×40 .

The temperature distribution in the left-up corner of this problem is shown in the Fig. D.2(a). Because the conductivities of the external is very large, the temperature of exterior region contacted with the interface is the same as the temperature of the boundaries as $T = 0$. Because the ratio of width to height of the interior rectangular is large, the temperature profile along the symmetric line ($y = x$) can be seen as the solution of the one-dimensional heat conduction. The temperature of the exterior region contacted with the interface is zero. Then the temperature of the interior region contacted with the interface is $[[T]] = R_j q_n$. The q_n is the heat flux across the interface along the symmetric line. The value of $q_n = S\sqrt{2}/2$ and $[[T]] = 5\sqrt{2}$. The analytical solution of temperature distribution along the symmetric line is:

$$T(x) = -10(\sqrt{2}x)^2 + 100\sqrt{2}(\sqrt{2}x) - 455\sqrt{2}$$

(a) Temperature distribution

(b) Comparison of the results between numerical and analytical along the symmetric line $y = x$

Figure D.2: Two dimensional heat conduction problem with a rectangular inside.

The comparison between the numerical solution and analytical solution is shown in Fig. D.2(b). The two results agree with each other.

D.0.6 Two dimensional heat conduction in two homogenous materials with a circle inside

The third problem is two-dimensional heat conduction with a circle sub-domain inside. The computational domain is $[-0.5, 0.5] \times [-0.5, 0.5]$. The interface is defined by the circle $x^2 + y^2 = 0.04$. The region one is defined inside the circle and the region two defined outside. At the interface, the contact resistance is $R_j = 0.5$. The thermal conductivities are $k_1 = 1$ and $k_2 = 1000$, respectively. Dirichlet's conditions, $T = 0$, are defined at the boundaries. There is heat generation in the sub-domain one as $S = 20$.

Similar as the previous problem, because the conductivities of the sub-domain is very large, the temperature of region two contacted with the interface is the same as the temperature of the boundaries as $T = 0$. Then the temperature of the region one contacted with the interface is $[[T]] = R_j q_n$. The q_n is the heat flux across the interface, which can be calculated as $q_n = rS/2$, where r is the radius of the contact (interface). Then $[[T]] = R_j rS/2 = 1$. Then this problem can be solved in the cylindrical coordinate analytically. The solution of temperature inside the region one is $T = 1 + 5(0.04 - x^2 - y^2)$ in rectangular coordinate. The result by numerical method is shown in Fig. D.3(a). The grid size is 40×40 . Fig. D.3(b) compares the temperature at the line $y = 0$ with the analytical result. The result obtained by numerical method agrees with the analytical solution.

(a) Temperature distribution

(b) Comparison of the results between numerical and analytical along the symmetric line $y = x$

Figure D.3: Two dimensional heat conduction problem with a circle inside.

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