AC Electro-osmotic Pumping for Microfluidic Systems

A dissertation submitted to the
SWISS FEDERAL INSTITUTE OF TECHNOLOGY
ZURICH

for the degree of
Doctor of Sciences

presented by
BRIAN PATRICK CAHILL
BE, University College Dublin
MEng, Dublin City University
born July 10th, 1974
citizen of Dublin, Ireland

accepted on the recommendation of
Prof. Dr. A. Stemmer, examiner
Prof. Dr. O. J. F. Martin, co-examiner
Dr. H. F. Knapp, co-examiner

Zurich, 2005
Acknowledgements

This thesis is the result of my research at the Nanotechnology Group of the Swiss Federal Institute of Technology Zurich (ETHZ).

It is a great pleasure for me to thank Prof. Dr. Andreas Stemmer for supervising this doctoral thesis, for giving me the opportunity to work in such a stimulating interdisciplinary research environment and for his interest and support during the course of the project.

Much appreciation is due to Prof. Dr. Olivier Martin, head of the Nanophotonics and Metrology Laboratory of the Swiss Federal Institute of Technology Lausanne (EPFL), for acting as co-referee of this thesis and for inspiring and fruitful discussions.

I would like to thank Dr. Helmut Knapp, leader of the Microsystem Technology Group of CSEM Alpnach, for accepting the role of co-referee of this thesis. In this role he contributed many important insights. Furthermore he was very generous with his expertise at the very start of my studies in Zurich.

I wish to acknowledge the valuable and much appreciated col-
laboration with Dr. Laura Heyderman and Dr. Jens Gobrecht of the Laboratory for Micro- and Nanotechnology of the Paul Scherrer Institut. Their fabrication of electrode structures was indispensable to the success of this thesis.

Very special thanks go to Guy Birrer for his enthusiasm and skill in electric circuit design.

I thank Dr. David Juncker and Richard Stutz of IBM Zurich Research Laboratory for coating my samples with tantalum pentoxide.

I owe much to all the members of the Nanotechnology Group for their suggestions, inspiration, encouragement and friendship: Dr. Yury Belyaev, Claudia Brunner, Dr. Markus Brunner, Ralph Friedlos, Dr. Jan Frohn, Altan Gürel, Dr. Daniel Häfliger, Stefan Lengweiler, Dr. Patrick Mesquida, Nicola Naujoks, Dr. Bohuslav Rezek, Miho Sakai, Marianne Schindler, Dr. Georg Schitter, Dr. Robert Stark, Dr. Roxana Stoenescu, and Dr. Laurence Vindevoghel.

Finally, special thanks go to my parents and to Rónán, Eamonn, and Claire for their constant encouragement and support.
Table of Contents

Abstract ix
Kurzfassung xi
List of Symbols xiii

1 Introduction 1
   1.1 Motivation and Objective 1
   1.2 Electric Double Layer Basics 2
   1.3 Fluid Flow in AC Electric Fields 6
   1.4 AC Electro-osmosis Excited by Traveling Waves 8
   1.5 Thesis Outline 11

2 AC Electro-osmotic Flow driven by Traveling Waves 13
   2.1 Introduction 13

AC Electro-osmotic Pumping for Microfluidic Systems
AC Electro-osmotic Pumping for Microfluidic Systems
4 Flow Profile over Traveling Wave Electrodes

4.1 Basic model and governing equations

4.2 Numerical Solution of the Potential Distribution

4.2.1 Electrical Solution

4.3 Profile of Fluid Flow

4.3.1 Fourier Components of Fluid Flow

4.3.2 Results

5 AC Electro-osmotic Flow over Interdigitated Electrodes

5.1 Introduction

5.2 Working Principles of Device

5.3 Materials and Methods

5.3.1 Microfabrication of Interdigitated Electrode Structures

5.3.2 Deposition of an insulating layer

5.3.3 Electrical Connections

5.3.4 Details of Experimental Setup

5.4 Experiments on Interdigitated Electrodes

5.5 Discussion

5.6 Conclusion

6 Conclusions

6.1 Summary

6.2 Outlook

6.2.1 Generation of True Plug Flow

6.2.2 Application of AC Electro-osmosis in Micro Fuel Cells
<table>
<thead>
<tr>
<th>viii</th>
<th>Table of Contents</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bibliography</td>
<td>87</td>
</tr>
<tr>
<td>A. Electrical Circuits</td>
<td>97</td>
</tr>
<tr>
<td>Curriculum Vitae</td>
<td>100</td>
</tr>
</tbody>
</table>

AC Electro-osmotic Pumping for Microfluidic Systems
Electro-osmotic flow over micro-electrodes on application of alternating-current electric fields, ac electro-osmotic flow, has recently become a field of great interest for fluid handling in microfluidic systems. The method holds out the possibility of electro-osmotic pumping that can cause plug flow at applied potentials low enough for the method to be easily integrated into lab-on-a-chip device. Also, electro-osmosis is a surface generated flow that outperforms externally generated pressure flow when pumping in microchannels.

In this thesis, ac electro-osmotic flow of an aqueous electrolyte on application of alternating electric fields is described. Two electrode structures have been developed to cause ac electro-osmosis. The first takes the form of a four electrode spiral to which a four-phase traveling wave signal is applied. Depending on the frequency of the applied electric field, the interaction of the charge density of the electric double layer and the tangential electric field leads to fluid flow in the direction of the traveling wave. The second takes the form of an interdigitated electrode structure. Alternating potentials of the same frequency and
amplitude but of differing phase are applied to neighbouring electrodes. The direction of flow can be changed by varying the phase difference between these signals. Experimental evidence that streaming takes place on application of a traveling wave of potential by tracing the movements of fluorescent latex beads over a spiral electrode structure is provided.

Two analytical models are derived that describe flow due to application of a traveling wave as a function of the amplitude of the applied electric potential, the signal frequency, and the material properties of the system. The first is based on a capacitative model and is limited to frequencies much lower than the double layer relaxation frequency. The second is an analytical solution of the electrokinetic equations and is also valid at higher frequencies. In addition, a numerical simulation has been developed, that allows the flow profile over discrete electrodes to be simulated.
Kurzfassung

Der elektro-osmotische Fluss über Mikroelektroden durch das Anlegen elektrischer Wechselfelder (AC elektro-osmotischer Fluss) ist in den letzten Jahren auf großes Interesse für die mikrofluidische Handhabung von Flüssigkeiten gestossen. Mit dieser Methode kann durch elektro-osmotisches Pumpen eine Pfropfenströmung erzeugt werden, wobei die angelegten Potentiale so niedrig sind, dass die Methode in einem Lab-on-a-Chip leicht integriert werden kann. Ausserdem ist die Elektro-osmose ein oberflächenerzeugter Fluss, der den extern erzeugten Druckfluss beim Pumpen in Mikrokanälen an Leistung übertrifft.

In der vorliegenden Dissertation wird die Erzeugung eines elektro-osmotischen Flusses eines wässrigen Elektrolyts durch das Anlegen eines elektrischen Wechselfeldes beschrieben. Zwei Elektrodenstrukturen werden entwickelt, um AC Elektro-Osmose zu erzeugen. Die erste Struktur hat die Form einer Vierelektrodenspirale, an die ein vierphasiges, wanderndes Wellensignal angelegt wird. Abhängig von der Frequenz des angelegten elektrischen Wechselfeldes führt die Interaktion zwischen der Ladungsdichte der elektrischen Doppelschicht und dem

AC Electro-osmotic Pumping for Microfluidic Systems
tangentialen elektrischen Feld zu einer Strömung in Richtung der wandernden Welle.


List of Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c$</td>
<td>concentration</td>
</tr>
<tr>
<td>$C_{Stern}$</td>
<td>capacitance per unit area of the Stern layer</td>
</tr>
<tr>
<td>$C_{ins}$</td>
<td>capacitance per unit area of the insulating layer</td>
</tr>
<tr>
<td>$C_{edl}$</td>
<td>capacitance per unit area of the electric double layer</td>
</tr>
<tr>
<td>$C_{sum}$</td>
<td>series summation of capacitances, $C_{ins}$, $C_{Stern}$, and $C_{edl}$</td>
</tr>
<tr>
<td>$D$</td>
<td>diffusion coefficient</td>
</tr>
<tr>
<td>$D$</td>
<td>displacement field vector</td>
</tr>
<tr>
<td>$Du$</td>
<td>Dukhin number</td>
</tr>
<tr>
<td>$e$</td>
<td>electron charge</td>
</tr>
<tr>
<td>$E$</td>
<td>electric field vector</td>
</tr>
<tr>
<td>$E_{t}$</td>
<td>tangential electric field</td>
</tr>
<tr>
<td>$e_x$</td>
<td>unit vector in the $x$ direction</td>
</tr>
<tr>
<td>$e_y$</td>
<td>unit vector in the $y$ direction</td>
</tr>
<tr>
<td>$f_j$</td>
<td>is the flux density of ions of type $j$</td>
</tr>
<tr>
<td>$G$</td>
<td>Green’s function</td>
</tr>
<tr>
<td>$i$</td>
<td>$\sqrt{-1}$</td>
</tr>
<tr>
<td>$J$</td>
<td>electrical current</td>
</tr>
<tr>
<td>$k$</td>
<td>Boltzmann’s constant</td>
</tr>
<tr>
<td>$k_y$</td>
<td>propagation constant of traveling wave</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
</tr>
<tr>
<td>$L_c$</td>
<td>characteristic length</td>
</tr>
<tr>
<td>$n$</td>
<td>unit vector normal to the surface</td>
</tr>
<tr>
<td>$n_j$</td>
<td>number density of ions of type $j$</td>
</tr>
<tr>
<td>$n_j^\infty$</td>
<td>number density of ions of type $j$ in the bulk fluid</td>
</tr>
<tr>
<td>$p$</td>
<td>fluid pressure</td>
</tr>
<tr>
<td>$Re_l$</td>
<td>electric Reynolds number</td>
</tr>
<tr>
<td>$t$</td>
<td>time</td>
</tr>
<tr>
<td>$T$</td>
<td>absolute temperature</td>
</tr>
<tr>
<td>$t_{ins}$</td>
<td>thickness of the insulating layer</td>
</tr>
<tr>
<td>$t_{Stern}$</td>
<td>thickness of the Stern layer</td>
</tr>
<tr>
<td>$u$</td>
<td>fluid velocity vector</td>
</tr>
<tr>
<td>$u$</td>
<td>fluid velocity in $y$ direction</td>
</tr>
<tr>
<td>$U$</td>
<td>average slip velocity</td>
</tr>
<tr>
<td>$v$</td>
<td>fluid velocity vector</td>
</tr>
<tr>
<td>$v$</td>
<td>fluid velocity in $x$ direction</td>
</tr>
<tr>
<td>$V$</td>
<td>potential</td>
</tr>
<tr>
<td>$v_{slip}$</td>
<td>electro-osmotic slip velocity</td>
</tr>
<tr>
<td>$z$</td>
<td>ion valence</td>
</tr>
<tr>
<td>$\Delta$</td>
<td>distance from the dielectric surface to the edge of the electric double layer</td>
</tr>
<tr>
<td>$\Delta \theta$</td>
<td>phase difference</td>
</tr>
<tr>
<td>$\delta$</td>
<td>$t_{ins} \varepsilon_2 \kappa / \varepsilon_1$</td>
</tr>
<tr>
<td>$\delta n_j$</td>
<td>small sinusoidal disturbance to the number density of ions of type $j$</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>dielectric constant</td>
</tr>
<tr>
<td>$\varepsilon_1$</td>
<td>dielectric constant of insulating layer</td>
</tr>
<tr>
<td>$\varepsilon_2$</td>
<td>dielectric constant of water</td>
</tr>
<tr>
<td>$\varepsilon_{Stern}$</td>
<td>dielectric constant of the Stern layer</td>
</tr>
<tr>
<td>$\varepsilon_0$</td>
<td>permittivity of free space</td>
</tr>
<tr>
<td>$\zeta$</td>
<td>electrokinetic potential</td>
</tr>
<tr>
<td>$\eta$</td>
<td>fluid viscosity</td>
</tr>
<tr>
<td>$\theta$</td>
<td>phase</td>
</tr>
<tr>
<td>$1/\kappa$</td>
<td>Debye length</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>wavelength of traveling wave electrode structure</td>
</tr>
<tr>
<td>$\rho_f$</td>
<td>fluid density</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>conductivity</td>
</tr>
<tr>
<td>$\sigma_D$</td>
<td>surface charge density associated with double layer</td>
</tr>
<tr>
<td>$\sigma_E$</td>
<td>surface charge density on electrode surface</td>
</tr>
</tbody>
</table>

AC Electro-osmotic Pumping for Microfluidic Systems
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma_{Tot}$</td>
<td>sum of $\sigma_D$ and $\sigma_E$</td>
</tr>
<tr>
<td>$\tau$</td>
<td>electric double layer relaxation frequency</td>
</tr>
<tr>
<td>$\varphi$</td>
<td>potential satisfying Poisson's equation</td>
</tr>
<tr>
<td>$\phi$</td>
<td>potential satisfying Laplace's equation</td>
</tr>
<tr>
<td>$\phi_u(x,y)$</td>
<td>potential due to a uniform grid of source lines of unit charge</td>
</tr>
<tr>
<td>$\Phi$</td>
<td>potential just outside the electric double layer</td>
</tr>
<tr>
<td>$\Phi_y$</td>
<td>$\partial \Phi / \partial y$</td>
</tr>
<tr>
<td>$\psi$</td>
<td>real amplitude of the potential</td>
</tr>
<tr>
<td>$\hat{\psi}$</td>
<td>complex amplitude of the potential</td>
</tr>
<tr>
<td>$\Psi$</td>
<td>stream function</td>
</tr>
<tr>
<td>$\Psi_{OHP}$</td>
<td>potential at the outer Helmholtz plane</td>
</tr>
<tr>
<td>$\Psi_{IHP}$</td>
<td>potential at the inner Helmholtz plane</td>
</tr>
<tr>
<td>$\omega$</td>
<td>radial frequency</td>
</tr>
<tr>
<td>$\omega_c$</td>
<td>characteristic frequency</td>
</tr>
<tr>
<td>$\Omega$</td>
<td>normalised frequency</td>
</tr>
<tr>
<td>$\nabla$</td>
<td>gradient operator</td>
</tr>
<tr>
<td>$^*$</td>
<td>diacritical mark signifying a complex quantity</td>
</tr>
</tbody>
</table>
Chapter 1

Introduction

1.1 Motivation and Objective

The philosophy of lab-on-a-chip systems is to use microtechnology to miniaturise laboratory instruments in the fields of biology and chemistry. In the last 40 years, microfabrication revolutionised the field of microelectronics and offers similar advantages to lab-on-a-chip technology. Highly integrated and multifunctional systems on-chip can be developed that can be mass fabricated at low cost. Reducing cost allows devices to be used disposably.

Lab-on-a-chip systems require controllable pumps capable of pumping small volumes that can be integrated into microsystems. Many of the pumps used in microsystems require the use of moving parts [SHOJI94]. There is widespread interest in the use of

AC Electro-osmotic Pumping for Microfluidic Systems
Introduction

electro-osmotic flow as a non-contact pumping technique using dc electric fields in lab-on-a-chip systems [Devas'pathy2002, Herr2000, Santiago2001, Schasfoort99]. A drawback of dc electro-osmotic flow is that it requires the application of relatively high potentials. Low-potential techniques that can be operated using battery power will enable the integration of electro-osmosis into lab-on-a-chip devices to be optimized, making the systems cheaper and more portable [Brask2003, Takamura2003]. The emergence of microfluidic devices has driven research into electro-osmotic streaming effects over charge-modulated surfaces [Ajdari95, Ajdari96, Ajdari2002A, Stroock2000, Long99, Nadal2002] and mixing of fluids flowing over grooved surfaces [Stroock2002A, Stroock2002B].

1.2 Electric Double Layer Basics

The electric double layer is a layer of ions that forms at an electrified interface with a characteristic length given by the Debye length $1/\kappa$, that can be expressed in terms of the diffusion coefficient $D$, the conductivity $\sigma$, and the dielectric constant of the fluid $\varepsilon$:

$$\kappa^2 \approx \frac{\sigma}{\varepsilon D}.$$  \hspace{1cm} (1.1)

In the bulk fluid, at distances from the solid liquid interface greater than $1/\kappa$, the net charge density is zero. In general, protonation, deprotonation, adsorption and other reaction equilibria define a net charge density on a surface in contact with an electrolyte. Gouy and Chapman independently developed a method to solve the Poisson equation at a charged interface by using the Boltzmann distribution to describe the distribution of ions in the area where the double layer is composed of a diffuse layer and a Stern layer.

Stern developed a model of the double layer with two layers that takes the effect of specific adsorption to the surface into account. The inner Helmholtz plane (IHP) is characterised by the adsorption of counterions to the surface. The outer Helmholtz plane (OHP) is the clos-
Fig. 1.1: The potential distribution in the double layer as a function of distance from the surface is superimposed over a schematic representation of the double layer according to the theory of Stern, Gouy, Chapman and Grahame. Illustration not to scale.

The closest distance that coions can approach the surface. The Stern layer is the area between these two Helmholtz planes and acts as a kind of molecular capacitor, where the capacitance per unit area is given by $C_{\text{Stern}} = \epsilon_{\text{Stern}}/t_{\text{Stern}}$, where $\epsilon_{\text{Stern}}$ and $t_{\text{Stern}}$ are the dielectric constant and thickness of the Stern layer respectively. The potential difference across the capacitor is given by the difference between the potential at the OHP $\Psi_{\text{OHP}}$ from that at the IHP $\Psi_{\text{IHP}}$. The dielectric constant of the Stern layer is lower than that in the bulk fluid because the polarisability of water molecules is significantly reduced in this region.

Many common double layer measurements techniques involve electrokinetics, the combination of double layer formation, a tangential electric field, and fluid flow. There are two general modes of
electrokinetic measurement: electro-osmotic flow and streaming current [Dukhin73, Hunter2001, Lyklema95].

Electro-osmosis is an electrokinetic phenomenon, in which ions in solution migrate in the presence of an electric field, causing a body force on the liquid that results in fluid flow. Net flow requires charge separation; that is, that the local net charge density is non-zero. The formation of the electric double layer results in such charge separation at a charged interface and applying an electric field in a direction tangential to the interface causes electro-osmotic flow [Hunter2001, Karniadakis2002, Lyklema95].

In electro-osmosis, the interaction of the electric double layer with an imposed electric field causes fluid flow. Streaming current is the opposite of this, it is an ionic current caused by fluid flow transporting the electric double layer charge. Thus, flow in a glass capillary causes a potential difference between the two ends of the capillary.

The viscosity of water near a surface increases from an infinite value at the surface to the bulk value at a distance of some one or two molecules from the surface. This variation in viscosity can be described by a two layer system. The first layer, that closest to the surface, is hydrodynamically immobile, i.e., has infinite viscosity. The second layer, the diffuse layer, begins at the shear plane where the viscosity can be considered equal to the bulk value and ends at the slip plane where any electro-osmotic flow reaches its slip value. The electrokinetic potential \( \zeta \) is the potential in the shear plane and arises in measurements by electrokinetic means, e.g., capillary electro-osmosis, streaming potential, or electrophoresis. The electrokinetic potential can be measured through the two electrokinetic phenomena: electro-osmosis and streaming current. In this way, it is much easier to quantify \( \zeta \) than it is to measure the absolute surface potential. The use of bulk values in the diffuse layer is generally accepted for the most relevant material constants: viscosity, dielectric constant, and ion mobility.

The mobility of ions in the region closest to the surface is still a
matter of some confusion. Conduction in this region has been dubbed "anomalous" but has been shown to significantly affect surface conductivity and electroacoustic measurements. While the exact position of the shear plain is one of the main unknowns of surface and interface science, the electrokinetic potential can be consistently measured by electrokinetic measurements.

The electrokinetic potential is a function of pH and ion concentration. Only at very high electrolyte concentrations is the double layer thickness less than the distance between the shear plane and the wall. The pH dependence of the electrokinetic potential is caused by the competitive adsorption of anionic (acidic) and cationic (basic) groups and their respective concentration in the electrolyte (pH). By changing the pH value of the electrolyte the net surface charge density can be positive or negative. At the isoelectric point the surface charge density is zero. Fig. 1.2 shows how the electrokinetic potential varies with concentration. For the highest concentration, $c_3$, the isoelectric point is reached.

The Smoluchowski equation [HUNTER2001] explains how the interaction of the surface charge density $\sigma_D$ caused by the formation of the electric double layer at an interface, with an electric field tangential to that interface $E_t$ causes electro-osmotic flow with slip velocity $v_{\text{slip}}$:

$$v_{\text{slip}} = \frac{\sigma_D E_t}{\kappa \eta}, \quad (1.2)$$

where $\eta$ is the fluid viscosity. The tangential electric field is located at the boundary between the electric double layer and the bulk fluid.

The magnitude of AC electro-osmotic flow is determined by the time-average of the multiplication of $\sigma_D$ and $E_t$. On application of an alternating potential to an electrode system, these two terms are both sinusoids and $v_{\text{slip}}$ is determined by the magnitude of these two quantities but also the phase difference between them.

Although a certain part of $\sigma_D$ is due to the equilibrium electrokinetic potential, the time-average slip velocity resulting from the multiplication of this component of $\sigma_D$ and $E_t$ is zero. Only the sinusoidal

---

AC Electro-osmotic Pumping for Microfluidic Systems
1 Introduction

Fig. 1.2: Potential, $\Psi$, plotted against three concentrations, $c_1$, $c_2$ and $c_3$, where $c_3 > c_2 > c_1$. The electrokinetic potential decreases with increasing electrolyte concentration. Illustration not to scale.

perturbation due to the applied ac signal causes time-averaged fluid flow.

1.3 Fluid Flow in AC Electric Fields

The arrangement of colloids on application of alternating electric fields has recently been observed [TRAU97, YEH97]. Subsequently, experimental studies were made of circulatory flow patterns in aqueous electrolytes over microelectrodes on application of alternating electric fields [RAMOS99A, RAMOS99B, GREEN2000, GREEN2002, NADAL2002]. Various models [TRAU97, GREEN2002, GONZALEZ2000, NADAL2002] explained this as a form of electro-osmotic flow which became known as alternating current (ac) electro-osmosis. Ajdari suggested using asymmetric electrode structures to drive unidirectional ac electro-osmotic flow [AJDARI2000] and working systems have been implemented [BROWN2001, RAMOS2003, STUDER2002, MPHOLO2003]. Most of these studies have dealt with the frequency-dependent impedance at fre-
quencies much lower than the double layer relaxation frequency and the flow was explained by a combination of equilibrium double layer theory and the Smoluchowski equation [Ajdari2000, Green2002, Ramos99a, Ramos2003]. González et al. [González2000] also dealt with the relaxation of the double layer at frequencies of the order of the double layer relaxation frequency by solving the electrokinetic equations using a matched asymptotic expansion method.

Some work has been carried out in the field of electrical engineering to describe electrohydrodynamic pumping of insulating liquids, such as Freon, transformer oil, and corn oil, over traveling-wave electrodes [Ehrlich82, Choi95, Washabaugh89] on application of ac electric fields at frequencies in the range of the double layer relaxation frequency. Charge sources in low conductivity fluids generally result from the concentration of impurities, which are either molecular in scale or large particles and can be ionic [Harvey2002]. Ehrlich and Melcher [Ehrlich82] modeled a type of electro-osmotic streaming in the electric double layer due to traveling-wave excitation for bipolar charge carriers subject to generation and recombination by examining the electrokinetic equations and obtaining both analytical solutions, for certain limiting cases, and a more generally applicable computational solution. They describe a type of streaming caused by the interaction of the electric field with the net charge associated with the electric double layer at a solid-liquid interface as the applied traveling wave approaches the double layer relaxation frequency of the liquid medium.

Another type of electrohydrodynamic pumping at frequencies in the range of the double-layer relaxation frequency has also been reported for the case of the interaction of a traveling-wave electric field and an imposed thermal gradient in a fluid. The coupling of this thermal gradient to the temperature dependence of conductivity and dielectric constant leads to local field inhomogeneities that are strong enough to generate deviations from electroneutrality within the bulk of the fluid and leads to convective flow. This phenomenon was first described for insulating fluids [Bart90, Melcher66, Melcher67] and later extended to aque-
ous electrolytes [Fuhr92, Fuhr94, Gimsa97, Müller93]. In aqueous electrolytes, the imposed traveling-wave electric field near the electrodes leads to a local temperature rise so that it is no longer necessary to externally impose a thermal gradient. The fluid flow took place in a direction opposite to that of the traveling-wave electric field, although Fuhr et al. [Fuhr94] and Gimsa et al. [Gimsa97] observed another type of fluid flow taking place in the direction of the traveling-wave electric field. No detailed study of this second phenomenon was performed, which both groups explained by means of reference to Ehrlich and Melcher [Ehrlich82]. It is likely that the second phenomenon was a form of ac electro-osmosis.

1.4 AC Electro-osmosis Excited by Traveling Waves

In this thesis we present experimental results showing how a traveling wave potential can excite electro-osmotic flow [Cahill2004a]. Traveling wave electrode arrangements have previously found application in electrically driven fluid flow [Washabaugh89, Bart90, Melcher66, Fuhr92] and particle handling [Hagedorn92, Moesner96].

Fig. 1.3 is a simplified explanation of how traveling waves cause directed electro-osmotic flow for a traveling wave traveling from left to right. On application of a potential to the electrodes, the formation of the electric double layer results in the accumulation of ions close to the electrodes so that the surface charge density is non-zero. The applied potential also results in an electric field penetrating into the bulk fluid, and the tangential part of this electric field interacts with the double layer charge to cause electro-osmotic flow. The magnitude of electro-osmotic flow is determined by the interaction of the electric double layer charge with the electric field, more specifically, the electric field tangential to the interface. The magnitude and phase of these two quantities is dependent on the frequency of the applied traveling wave. The frequency-dependent phase difference between the signal applied to the electrodes.
and the resultant electric field in the electrolyte is more complex than shown here but to understand the phenomenon it is more important to note the phase difference between the electric double layer and the tangential electric field.

Fig. 1.3 (a) shows the situation at very low frequencies, the double layer charge and tangential electric field are 90° out of phase and no directed flow can take place. Also the tangential component of the electric field is attenuated considerably by the formation of the double layer. No time average flow takes place because the average of flow over the surface is zero.

As the frequency of the applied traveling wave electric field approaches a certain characteristic frequency \( \omega_c \), as shown in Fig. 1.3 (b), the phase difference between the electric double layer and the tangential electric field decreases so that a time-averaged flow in the direction of motion of the traveling wave takes place. Also the tangential electric field increases in strength and the electric double layer charge density may decrease. The tangential component of the electric field over electrodes 1 and 2 points towards the right hand side and the positive ions surrounding these electrode 2 migrate from left to right. There is a lag between the formation of the electric field and the tangential electric field, the fluid flow over electrode 1 is not equal and opposite to the fluid flow over electrode 2. The development of fluid flow above electrodes 3 and 4 is analogous to that over electrodes 1 and 2 resulting in fluid flow in the same direction.

Fig. 1.3 (c) shows how the traveling wave moves across the surface, as the time increases by a quarter period of the traveling wave signal applied to the electrodes. This shows that the velocity over each electrodes varies from a maximum to a minimum but that time-averaged flow takes place in the same direction over all electrodes with a velocity that depends on the phase difference between the tangential electric field and the double layer charge density as well as the absolute value of these two quantities. The directionality of the flow may be controlled externally by changing the direction of travel of the traveling-wave electric
Fig. 1.3: Diagram explaining the mechanism of electro-osmotic flow due to the application of a traveling wave that travels from left to right. A plus/minus sign on an electrode signifies that a positive/negative potential is instantaneously applied to the electrode. A plus/minus sign above the insulating layer signifies that the electric double layer (EDL) has a surplus of positive/negative ions. These illustrations show uniform field lines although the field lines will be quite non-uniform in practice. The density of the field lines indicates the strength of the field. (a) No time-averaged electro-osmotic flow takes place at frequencies much lower than the characteristic frequency $\omega_c$. (b) At frequencies for which the formation of the electric double layer lags the signal applied to the electrodes, the interaction between the surface charge density associated with the electric double layer and the tangential electric field causes non-zero time-averaged fluid flow. (c) The same conditions as in (b) except that time is increased by a quarter period of traveling wave signal applied to the electrodes, corresponding to one step of a square-wave signal.
In a further step, we present a method for exciting ac electro-osmotic flow above interdigitated electrodes [CAHILL2004b]. The use of asymmetric interdigitated electrode structures to pump water by ac electro-osmosis results in flow that is limited to pumping in one direction at least when low potentials are applied. We extend the principle of traveling wave electro-osmotic flow to more practical interdigitated electrodes by applying phase-shifted signals to an interdigitated electrode structure and by including a ground layer. The ground layer helps define the phase difference between the electrodes and by applying potentials with a defined phase difference to adjacent electrodes the direction of flow can be controlled by varying the phase difference. The use of an interdigitated structure results in making the method much more simple to integrate into a working lab-on-a-chip device.

1.5 Thesis Outline

Chapter 2 is dedicated to the preparation of spiral electrode structures and reporting the experimental results of the traveling-wave-induced motion of fluorescent latex beads above these spiral electrode structures. In chapter 3, two analytical models are derived that describe electro-osmotic flow on application of a traveling wave of potential. The first model describes the electro-osmotic slip velocity by means of a capacitative model of the equilibrium double layer. This model is limited to frequencies much lower than the double layer relaxation frequency. The second model is based on a solution of the electrokinetic equations that is valid for frequencies of the order of the double layer relaxation frequency. Both models give the same results at frequencies much lower than the double layer relaxation frequency. We relate the experimental results to the second model. We show how the short wavelength of the traveling-wave electrode structure, 6 μm, enables fluid streaming to take place on applying signals with relatively low amplitudes, below 500 mV. In chapter 4, the electro-osmotic flow is modeled by the charge simulation method so that the geometry of the electrode structure can be
taken into account. In chapter 5, experimental results describing electro-osmotic flow above interdigitated electrode structures on application of phase shifted signals are reported. A discussion, chapter 6, concludes the thesis.
Chapter 2

AC Electro-osmotic Flow driven by Traveling Waves

2.1 Introduction

In this chapter, experimental work describing ac electro-osmosis on application of traveling-wave potentials to a spiral electrode structure is presented. The use of a traveling wave allows the direction of flow to be controlled externally by changing the direction of travel of the travel-

\footnote{Parts of this chapter are also published in: B. P. Cahill, L. J. Heyderman, J. Gobrecht, and A. Stemmer, Electro-osmotic streaming on application of traveling-wave electric fields, Physical Review E 63, 036305 (2004).}

AC Electro-osmotic Pumping for Microfluidic Systems
The asymmetric interdigitated electrode structures that have been used to cause ac electro-osmotic flow [AjDari2000, Brown2001, Ramos2003, Studer2002, Mpholo2003] have the disadvantage that the direction of flow cannot be controlled externally.

2.2 Working Principles of Device

In section 1.4, we explained how traveling wave fields can cause electro-osmosis. Fig. 1.3 shows how ac electro-osmotic flow takes place over a traveling-wave electrode structure. The difference between Figs. 1.3 (a) and (b) is that the applied frequency approaches the relaxation frequency of the system in Fig. 1.3 (b) so that the electric field penetrates into the bulk fluid and the phase difference between the electric double layer charge and the tangential electric field becomes more conducive to non-zero time-averaged electro-osmotic flow. The frequency at which this relaxation occurs depends on two mechanisms as will be explained more fully in chapter 3. First there is a resistance-capacitance (RC) relaxation due to the series capacitance of electric double layer and insulation layer and the resistance of the fluid medium between the electrodes which results in an increase in the amplitude of $E_t$ and also a change in its phase angle. Second, the electric double layer has a characteristic relaxation time given by $\tau = \varepsilon/\sigma$. As the frequency approaches this relaxation frequency the surface charge density of the electric double layer drops and its formation begins to lag the applied signal. In chapter 3 it will be explained how the electric double layer relaxation need only be taken into account if the RC relaxation frequency is greater than or of the same order as the electric double layer relaxation frequency.
Fig. 2.1: (a) Schematic drawing of the spiral electrode structure, four electrodes are arranged in a spiral structure and numbered 1-4. (b) Scanning electron microscope image of the center of the spiral electrode structure. (c) Square-wave traveling-wave signals 1-4 that are applied to electrodes 1-4 as shown in (a).
2.3 Materials and Methods

2.3.1 Microfabrication of Electrode Structures

The electrode design was exposed in a 150 nm thick layer of PMMA on a silicon substrate coated with a 120 nm layer of silicon dioxide using a LEICA LION LV1 e-beam writer. This machine is equipped with continuous path control that allows structuring of large areas without stitching errors. Lines of various widths can be added using a defocused exposure [DAVID99]. The exposed areas were then transferred into metal using the following lift-off procedure; a 10 nm titanium/70 nm aluminum layer was deposited by evaporation. The thin layer of titanium provided good adhesion of the aluminum to the silicon substrate. Unwanted aluminum deposited on the PMMA was removed in acetone using ultra-sonic agitation.

The spiral structures, see Figs. 2.1(a) and 2.1(b), were 150 μm in diameter and consisted of four electrodes. The electrode lines were 750 nm wide and separated by 750 nm gaps. The wavelength λ of the traveling wave structure was 6 μm. A spiral configuration was chosen for the convenience of fabricating a traveling-wave electrode structure that does not require complicated interconnections. For ease of bonding, the four connecting lines (40 μm wide and 4 mm long) were placed symmetrically around the spirals with 100-μm-by-200-μm bonding pads at the outer end.

2.3.2 Deposition of an insulating layer

The use of aluminium electrodes necessitates the use of a protective insulation layer. Strong electric fields act to increase the temperature and at higher temperatures the thickness of the native oxide layer associated with aluminium increases, if the aluminium electrodes are in contact with water.

The structures were coated with a 50-nm-thick protective layer.
2.3 Materials and Methods

of a Teflon-like fluorocarbon. This was performed using a custom-built Plasma-Enhanced Chemical Vapour Deposition (PECVD) chamber [KNAPP99] using hexafluoropropene precursor gas (CF₃-CF=CF₂). The adhesion of the film was improved by removing hydrocarbon contamination from the surface in air plasma prior to coating.

2.3.3 Electrical Connections

Bonding wires were used to connect each of the four electrodes to a printed circuit board. The printed circuit board was connected by means of coaxial cables to a four-phase voltage supply.

2.3.4 Four-Phase Square Wave Generator

A purpose-built four-phase voltage supply was developed to generate square-wave-form traveling-wave signals in the range between 10 kHz and 5 MHz. Four-phase square-wave traveling-wave signals were applied to the four electrodes so that there was a 90° phase difference between the signals applied to each electrode. Fig. 2.1(c) shows the form of these square waves. Developing a square-wave signal generator requires much less expense than developing a four-phase sine-wave signal generator and also has the advantage of operating across a relatively wide bandwidth. The amplitude of the applied signal was measured using a Kikusui COR5521U 40 MHz digital oscilloscope.

2.3.5 Details of Experimental Setup

KCl solutions in the concentration range between 10⁻⁴ and 10⁻³ M were prepared and the conductivity of each was measured using a Knick 911 Conductivity Meter with a ZU 6985 4-electrode cell (Knick GmbH, Berlin, Germany). 200-nm-diameter Fluoresbrite carboxylate latex beads (Polysciences, Warrington, PA, USA) with yellow green fluorescence were suspended in the aqueous KCl solutions at concentrations.

AC Electro-osmotic Pumping for Microfluidic Systems
A microscope cover slip was placed over the spiral using double-sided-adhesive tape of 100-μm thickness as a spacer. After introducing the latex bead suspension into this cavity, bead movement was observed and images acquired by fluorescent light microscopy using a Nikon Eclipse 800 microscope and a Cohu CCD camera (Cohu Inc., San Diego, CA). Digital movies of the latex bead movement were made after focusing a 40× objective with 0.75 numerical aperture onto the electrode surface, thus only beads within the depth of field, less than 1 μm, could be observed. Measurements of the velocity of several beads were made for each frequency and excitation potential, and the average velocity and standard deviation were calculated. The velocity was estimated by measuring the distance traveled by a bead as tracked from the digital movie and dividing by the time separating these digital movie frames.

2.4 Experiments on Traveling Wave Spirals

The movement of fluorescent latex beads suspended in aqueous electrolytes with medium conductivities of 2.00 mS/m, 4.19 mS/m, and 8.36 mS/m over the spiral electrode structures was observed on application of a traveling wave of potential to the spiral electrode structure at frequencies of the order of the double layer relaxation frequency of the prepared electrolytic solutions. On applying a traveling-wave signal in the direction of the center of the spiral, the beads moved towards the center of the spiral. On reversing the direction of travel of the traveling-wave signal, the beads reversed direction and moved from the center towards the edge of the spiral. Thus it is clear that the traveling wave of potential was responsible for the movement of the latex beads. Motion of the beads was observed within a couple of microns of the surface of the chip.

Fig. 2.2 shows the summation of 20 thresholded frames. This
Fig. 2.2: Superposition of thresholded images showing the movement of fluorescent beads over the electrode structure. Illustrates the paths traveled by the fluorescent beads over the electrode structure. The beads are driven radially outwards in a straight line.

Experiments were carried out to evaluate the dependence of the velocity of the fluorescent latex beads on the signal frequency and applied potential. The velocity was measured for various signal frequencies at different applied potentials for each of the three electrolytic solutions. Fig. 2.3 shows three graphs, one for each of the three electrolytic solutions, that respectively show three curves for the velocity plotted against frequency at different applied potentials.

The general behaviour consistently shows that at low and high frequencies the velocity tends to zero while the peak velocity occurs at a frequency that is a little less than half the double layer relaxation frequency. The double layer relaxation time $\tau$ is related to the time required for the electric double layer to respond to a dynamic electric field and is given by $\tau = \varepsilon_2/\sigma$, where $\varepsilon_2$ is the dielectric constant of the electrolyte and $\sigma$ is the electrolyte conductivity. The lower conductivity electrolytes have higher velocities and the frequency of maximum velocity is lower for the same applied potential. For each electrolytic solution, the frequency of maximum velocity appears to be independent of the
Fig. 2.3: Experimentally measured values of the velocity of the fluorescent latex beads plotted against frequency at different applied potentials, as denoted on each graph. Figures (a), (b), and (c) present results obtained using aqueous electrolytes with the respective medium conductivities: 2.00 mS/m, 4.19 mS/m, and 8.36 mS/m. The fitted curves are to aid the eye.
2.4 Experiments on Traveling Wave Spirals

Measurement of the dependence of the velocity of the fluorescent latex beads on applied potential was made by first ascertaining the frequency of the peak velocity and then making a set of movies at this frequency for various applied potentials. Fig. 2.4 shows the dependence of the velocity on applied potential for an electrolytic solution with conductivity of 4.19 mS/m at 300 kHz. The velocity is plotted against the square of the potential applied to the electrodes and fitted to a straight line through the origin. Fig. 2.4 shows clearly that the velocity is directly proportional to the square of the applied potential. On increasing the applied potential above 500 mV, the latex beads were attracted to the electrode structure by positive dielectrophoresis [JONES95] so that it was not possible to study streaming at higher potentials.

![Graph showing velocity vs. applied potential squared](image)

**Fig. 2.4:** Experimentally measured values of the velocity of the fluorescent latex beads plotted against the square of applied potential with a medium conductivity of 4.19 mS/m (1/\(\kappa\) = 18.1 nm) and at an applied frequency of 300 kHz. A linear fit was applied showing the proportionality of velocity to the square of the applied potential, \(|\psi_a|^2\).
Chapter 3

Analytical Models

3.1 Introduction

In this chapter, we derive two analytical models to show how ac electro-osmosis is caused by a traveling wave of potential [CAHILL2004A]. Thereafter we compare these models with each other and with the experimental results presented in chapter 2.

\[\text{\textsuperscript{2}}\text{Parts of this chapter are also published in:}\]

AC Electro-osmotic Pumping for Microfluidic Systems
3.2 Basic Principles

The potential distribution is determined by capacitances of the system: (i) the insulating layer capacitance, (ii) the Stern layer capacitance, and (iii) the capacitance of the electric double layer. We choose to neglect the Stern layer capacitance but it could be easily included. We will show how the capacitance of an insulating layer affects the frequency at which electro-osmotic flow takes place.

Fig. 3.1 shows the important interfaces for our model. The interface between the substrate and the insulation layer, denoted by \( a \), is in the plane of the electrode structure that provides electrical excitation to our system. The interface between the insulation layer and the electrolyte is denoted by \( b \). The \( c \) plane is where the electric double layer can be considered to end and the fluid bulk begins, that is, where the volume charge density is zero and the field in the fluid obeys the Laplace equation. The subscripts \( a, b \) and \( c \) will be used throughout the chapter to denote a variable evaluated in the \( a, b, \) and \( c \) planes respectively. The \( x \) and \( y \) directions are, respectively, normal and parallel to these planes. We choose \( x \) to be zero in the \( b \) plane. The insulation of the electrodes serves to prevent Faradaic current, although, this analysis would also be applicable to perfectly polarizable electrodes.

We presume that the electrical potential at the dielectric interface and throughout the electrolyte takes the form of a sinusoidal wave traveling in the \( y \) direction:

\[
\psi(x, y, t) = \Re \left\{ \hat{\psi}(x) \exp (i (\omega t - k_y y)) \right\}, \tag{3.1}
\]

where \( \hat{\psi} \) is the complex amplitude of the potential, \( i \) denotes \( \sqrt{-1} \), \( \omega \) is the angular frequency of the applied traveling wave of potential, \( t \) is time, and \( k_y \) is the propagation constant of the traveling wave, that is, \( k_y = 2\pi/\lambda \), where \( \lambda \) is the wavelength of the traveling wave as shown in Fig. 1.3(b). The diacritical mark ^ signifies a complex quantity. We assume that the first harmonic of the Fourier series describing the square wave predominates.
3.3 Low-Frequency Model

![Diagram of a, b, and c planes]

Fig. 3.1: The a plane is the plane between the insulating layer and the substrate where the electrodes are located. The b plane is the plane between the insulating layer and the fluid. The c plane is where the electric double layer can be considered to end and the fluid bulk begins. The x / y directions are defined as normal / tangential to the interface respectively. The dashed line shows the extent of the electric double layer. The origin is in the b plane so that x = 0 at the interface between the insulating layer and the electrolyte. Δ is a distance normal to the surface of the dielectric layer at which the charge separation due to the electric double layer becomes negligible. \( t_{ins} \) is the thickness of the insulating layer.

The double layer relaxation frequency is the frequency for which \( \omega \tau = 1 \). It will prove useful to state the approximate width of the electric double layer, the inverse Debye length, in terms of the diffusion coefficient \( D \) and \( \tau \):

\[
\kappa^2 \approx \frac{1}{\tau D}.
\]  

(3.2)

3.3 Low-Frequency Model

We will first derive an expression for the electro-osmotic slip velocity in a fashion similar to Ajdari [AJDARI2000]. The following assumptions are made: (i) the frequency is much lower than the double layer relaxation frequency, \( \omega \tau \ll 1 \) so that the electric double layer is fully equilibrated, (ii) the Debye length is much smaller than the electrode dimensions, \( k_y \ll \kappa \), as we shall presume throughout this chapter and as applies to our experimental conditions, and (iii) the wavelength of the electrode structure is much longer than the insulating layer thickness,
kyt_{ins} \ll 1$, so the insulating layer can be viewed as "thin" allowing it to be approximated as a capacitor in series with the double layer.

The system can be described by two capacitors in series, the capacitance per unit area of the insulating layer $C_{ins} = \varepsilon_1/t_{ins}$ and the capacitance per unit area of the electric double layer $C_{edi} = \varepsilon_2 \kappa$. This presumes that the potential drop across the double layer is less than $kT/ze$, so that we can presume a linear relationship between the capacitance of the double layer and the inverse Debye length $\kappa$, where $z$ is the ion valence, $e$ is the electron charge, $k$ is Boltzmann's constant, $T$ is the absolute temperature. The sum of these capacitances is given by $C_{sum} = \varepsilon_2 \kappa/(1 + \delta)$ where $\delta = t_{ins} \varepsilon_2 \kappa/\varepsilon_1$.

Ohm's law describes ion transport in the bulk solution. Thus in the $c$ plane, Ohm's law applied in the direction normal to the surface gives:

$$n \cdot J = -\sigma \frac{\partial \psi}{\partial x} \bigg|_{c} = C_{sum} \frac{\partial (\psi_a - \psi_c)}{\partial t},$$

where $n$ is a unit vector normal to the surface.

The potential in the bulk fluid and in the $c$ plane obeys the Laplace equation, $\nabla^2 \psi = 0$, so that from the form of the traveling wave and if the potential decays to zero very far away from the surface, it can be shown that $\partial \psi/\partial x|_{c} = -k_y \psi_c$. By separation of variables it can be shown that

$$\hat{\psi}_c = \frac{\hat{\psi}_a}{1 - i(\omega_c/\omega)},$$

where the characteristic frequency $\omega_c$ is given by

$$\omega_c = \frac{\sigma k_y}{C_{sum}} = \frac{k_y (1 + \delta)}{\kappa T}.$$ 

The Smoluchowski equation [SMOLUCHOWSKI03] forms the basis of much work in electrokinetics and describes how the formation of the electric double layer gives rise to a surface charge density $\sigma_D$, which interacts with the tangential electric field $E_t$ to cause an electro-osmotic

AC Electro-osmotic Pumping for Microfluidic Systems
3.4 High-Frequency Model

We have chosen to develop a model that will be able to describe the effect of double layer relaxation on ac electro-osmotic flow because for

\[ v_{\text{slip}} = \frac{\sigma_d E_t}{\kappa \eta}, \]  

(3.6)

where the surface charge density is given by

\[ \sigma_d = C_{\text{sum}} (\psi_c - \psi_a) \]  

(3.7)

and the tangential electric field follows from the definition of the traveling wave,

\[ E_t = \Re \left\{ i k y \hat{\psi}_c(x) \exp(i(\omega t - k y y)) \right\}. \]  

(3.8)

The Smoluchowski equation is valid if the potential drop across the double layer is less than \( kT/\varepsilon \).

The time average of the product of two complex quantities is equal to half of the product of one of the quantities and the complex conjugate of the other. The time-averaged slip velocity \( \langle v_{\text{slip}} \rangle \) is given by

\[ \langle v_{\text{slip}} \rangle = \frac{\varepsilon_2 \left| \hat{\psi}_a \right|^2 \omega \tau}{2 \eta \kappa \left| \frac{1}{\kappa} + \frac{i \omega \tau}{k y} + \frac{\varepsilon_2}{\varepsilon_1} \right|^2}. \]  

(3.9)

For Eq. (3.9) to be valid \( \omega_c \) must be much less than the double layer relaxation frequency. Otherwise the assumptions of the model are not fulfilled because RC circuit approximation breaks down because the double layer is no longer in quasi equilibrium. The characteristic frequency \( \omega_c \) is the same as in Ajdari's model \[\text{[AJDARI2000]}\]. In principle, the ac electro-osmotic phenomenon is identical to that described by Ajdari, we describe a traveling wave here and Ajdari described a standing wave.

3.4 High-Frequency Model

We have chosen to develop a model that will be able to describe the effect of double layer relaxation on ac electro-osmotic flow because for
input data pertaining to our experiment $\omega_c$ is greater than the double layer relaxation frequency because of our use of an insulation layer and the relatively short wavelength of the electrode structure (6 $\mu$m). Although the insulation layer thickness (50 nm) is not much greater than the Debye length (12.8-26.3 nm), the dielectric constant is 40 times smaller than that of water so that $\delta$ is much greater than one (80 to 120) so that $\omega_c$ exceeds the double layer relaxation frequency.

3.4.1 Basic model and governing equations

The electrokinetic equations are a set of partial differential equations that relate electrical potential, ion densities, and fluid velocities in an electrolyte [Ehrlich82, Hunter2001, González2000, Isambert97, O'Brien83]. We shall presume that the fluid viscosity, dielectric constant and diffusion coefficient take the same value in the electric double layer as in the bulk fluid. We presume that the dielectric surface is intrinsically uncharged so that the formation of the electric double layer is a direct result of applying the traveling wave signal. We shall limit our analysis to low potentials, as we shall discuss in more detail below. The variation of ion density and potential in a conducting fluid at a dielectric interface on application of low amplitude ac potentials has previously been dealt with in the literature [Dukhin74, Trukhan63].

The ion conservation equation relates the rate of change of the number of ions per unit volume to the net rate at which ions enter that volume:

$$\frac{\partial n_j}{\partial t} = -\nabla \cdot f_j,$$

where $n_j$ is the number of ions of type $j$ per unit volume, and $f_j$ is the flux density. The flux density describes the number of ions that pass through a surface of a volume element per second and consists of terms related to diffusion, conduction and convection respectively:

$$f_j = -D_j \left( \nabla n_j + \frac{z_j e n_j}{kT} \nabla \psi \right) + n_j v,$$

where $D_j$ is the diffusion coefficient of ions of type $j$, $z_j$ is the valence of ions of type $j$, $v$ is the fluid velocity. The electric Reynolds number $Re_l$
3.4 High-Frequency Model

[MELCHER69] is the ratio of the characteristic times for electric double layer relaxation $\tau$ and for ion transport due to convection $1/(k_y v_y)$:

$$R_{el} = k_y v_y \tau,$$  \hspace{1cm} (3.12)

where $v_y$ is the fluid velocity in the $y$ direction. For the fluid velocity observed experimentally and the double layer relaxation times corresponding to the electrolytic solutions used in our experiments, the electric Reynolds number is much less than one. Hence, the double layer forms much more quickly than the convection can transport ions between neighboring electrodes, allowing us to neglect the charge convection term, $n_j v$, from Eq. (3.11).

Poisson's equation relates electrical potential to the local charge density in the region of the electric double layer:

$$\nabla^2 \psi = -\sum_{j=1}^{N} \frac{z_j e n_j}{\varepsilon_2},$$  \hspace{1cm} (3.13)

where $N$ is the number of ion types present in the electrolyte. If the local charge density is zero, Poisson's equation reduces to Laplace's equation:

$$\nabla^2 \psi = 0.$$  \hspace{1cm} (3.14)

For an incompressible fluid of uniform mass density and viscosity, fluid flow is governed by the incompressible Navier-Stokes equations:

$$\nabla \cdot v = 0 \text{ and } \rho_f \frac{\partial v}{\partial t} = \eta \nabla^2 v - \nabla p - \nabla \psi \sum_{j=1}^{N} z_j e n_j,$$  \hspace{1cm} (3.15)

where $\rho_f$ is the fluid density, $\eta$ is the fluid viscosity, and $p$ is the pressure. If the Reynolds number of the flow is much less than one, the inertial term of Eq. (3.16) may be considered negligible.

The analysis of electro-osmosis combined with non-uniform surface charge has previously been examined for colloids [ANDERSON85B] and for planar surfaces [HERR2000, NADAL2002, AJDARI95, AJDARI96].

AC Electro-osmotic Pumping for Microfluidic Systems
LONG99, ANDERSON85A]. If the surface charge varies over a distance that is much greater than the double layer, it is usual to decouple the problem into two problems: (i) inside the double layer the pressure gradient can be considered negligible so that the electro-osmotic slip velocity is given by the Smoluchowski equation and (ii) outside the double layer the net volume charge density is negligible so that the fluid dynamic problem can be solved using the electro-osmotic slip velocity as a boundary condition [ANDERSON89]. Our case is slightly different to these cases because the surface potential is a function of time and position at frequencies of the order of the double layer relaxation frequency.

We choose to deal with this problem by following the example of Anderson [ANDERSON85B] and considering flow in the direction normal to the surface inside the double layer to be negligible so that the vector components of Eq. (3.16) reduce to:

\[
\eta \frac{\partial^2 v_y}{\partial x^2} = \frac{\partial p}{\partial y} - \varepsilon_2 \nabla^2 \psi \frac{\partial \psi}{\partial y} \quad \text{and} \quad \quad \quad (3.17)
\]

\[
\frac{\partial p}{\partial x} = \varepsilon_2 \nabla^2 \psi \frac{\partial \psi}{\partial x} = \varepsilon_2 \left( \frac{\partial^2 \psi}{\partial x^2} - k_y^2 \psi \right) \frac{\partial \psi}{\partial x}. \quad \quad \quad (3.18)
\]

Eq. (3.18) can be integrated directly to obtain an expression for the pressure that can be used to state \( \frac{\partial p}{\partial y} \) as

\[
\frac{\partial p}{\partial y} = \varepsilon_2 \frac{\partial \psi}{\partial x} \frac{\partial^2 \psi}{\partial x \partial y} - \varepsilon_2 k_y^2 \psi \frac{\partial \psi}{\partial y}. \quad \quad \quad (3.19)
\]

### 3.4.2 Frequency-dependent ionic concentration in the electric double layer

In order to describe the local ion density, we choose to split it into two components, the ion density in the bulk fluid \( n_j^\infty \) and a small sinusoidal disturbance \( \delta n_j \):

\[
n_j(x, y, t) = n_j^\infty + \delta n_j(x, y, t), \quad \quad \quad (3.20)
\]

where \( \delta n_j \) takes the form of the applied traveling wave, \( \delta n_j = \Re \{ \delta \hat{n}_j(x) \exp (i (\omega t - k_y y)) \} \), \( \delta \hat{n}_j \) is the complex amplitude of \( \delta n_j \), and
3.4 High-Frequency Model

\[ \delta n_j < n_j^\infty. \] From Eqs. (3.10), (3.11), and (3.20), we obtain the following:

\[
\frac{\partial \delta n_j}{\partial t} = D_j \left( \nabla^2 \delta n_j + \frac{z_j e}{kT} ((n_j^\infty + \delta n_j) \nabla^2 \psi + \nabla \delta n_j \cdot \nabla \psi) \right). \quad (3.21)
\]

Considering an electrolyte, with ion densities, \( n_1 \) and \( n_2 \), and valences, \( z_1 \) and \( z_2 \), where the subscripts 1 and 2 represent cations and anions respectively, we obtain the following simultaneous equations:

\[
\mathbb{R}\left\{ i \omega \delta n_1 \exp(i(\omega t - k_y y)) \right\} = D_1 \left( \nabla^2 \delta n_1 + \frac{z_1 e}{kT} ((n_1^\infty + \delta n_1) \nabla^2 \psi + \nabla \delta n_1 \cdot \nabla \psi) \right) \quad \text{and} \quad (3.22)
\]

\[
\mathbb{R}\left\{ i \omega \delta n_2 \exp(i(\omega t - k_y y)) \right\} = D_2 \left( \nabla^2 \delta n_2 + \frac{z_2 e}{kT} ((n_2^\infty + \delta n_2) \nabla^2 \psi + \nabla \delta n_2 \cdot \nabla \psi) \right). \quad (3.23)
\]

By restricting ourselves to strong symmetrical electrolytes, we may relate the properties of ions of type 2 to those of ions of type 1. The diffusion coefficient of each type of ion is identical, \( D = D_1 = D_2 \), this can be considered true for KCl. The bulk concentration of both ions is the same: \( n_1^\infty = n_2^\infty = n_1^\infty \). The anions and cations possess charge of equal magnitude and opposite polarity, so that the valence is also opposite and equal: \( z_1 = -z_2 \). By introducing the following two substitutions,

\[
g = \frac{\delta n_1 - \delta n_2}{2} = \mathbb{R}\left\{ \hat{g}(x) \exp(i(\omega t - k_y y)) \right\} \quad \text{and} \quad (3.24)
\]

\[
h = \frac{\delta n_1 + \delta n_2}{2} = \mathbb{R}\left\{ \hat{h}(x) \exp(i(\omega t - k_y y)) \right\}, \quad (3.25)
\]

and by subtracting Eq. (3.23) from Eq. (3.22), we reduce these simultaneous equations to one differential equation:

\[
\mathbb{R}\left\{ i \omega \hat{g} \exp(i(\omega t - k_y y)) \right\} = D \left( \nabla^2 g + \frac{z_1 e}{kT} ((n_1^\infty + \hat{h}) \nabla^2 \psi + \nabla \hat{h} \cdot \nabla \psi) \right). \quad (3.26)
\]

---

AC Electro-osmotic Pumping for Microfluidic Systems
Fig. 3.2: (a) The component of the potential that is dropped across the Debye length $1/\kappa$, $\varphi$, is plotted against distance from the liquid-solid interface $x$. (b) The concentration of negative ions $n_2$ increases on application of a positive potential $\varphi_b$ inside the electric double layer while the concentration of positive ions $n_1$ drops. In the bulk fluid, the concentration of both returns to the bulk value $n^\infty$. (c) In the region of the double layer, $g$ is non zero, reflecting the net volume charge density of the electric double layer.

In Fig. 3.2 (a) the potential that is dropped across the electric double layer, $\varphi$, (b) the concentrations of positive and negative ions, $n_1$ and $n_2$, and (c) $g$ are respectively plotted against distance from the liquid-solid interface $x$. The net charge density is directly proportional to $g$ and is only significant inside the electric double layer.

At low applied potentials, $\delta n_1$ and $\delta n_2$ have equal amplitudes and are $180^\circ$ out of phase with each other, this requires that $g < n^\infty$, which restricts us to applying low potential as we shall discuss later. It also means that $h$ may be considered negligible throughout the electrical double layer and the bulk fluid. In addition, by inserting Poisson's
equation, Eq. (3.13), into Eq. (3.26) it can be shown that

\[ i\omega \hat{g} = D (\nabla^2 \hat{g} - \kappa^2 \hat{g}), \quad (3.27) \]

where the inverse Debye length \( \kappa \) [DEBYE23A, DEBYE23B] is described by

\[ \kappa^2 = \frac{2z^2 e^2 n^\infty}{\varepsilon_2 kT}. \quad (3.28) \]

Separation of variables further simplifies Eq. (3.27):

\[ \kappa^2 (1 + i\omega \tau) \hat{g} = \nabla^2 \hat{g} = \left( \frac{\partial^2 \hat{g}}{\partial x^2} - k_y^2 \hat{g} \right), \quad (3.29) \]

where the second term on the right hand side is the second derivative of \( g \) with respect to \( y \). Further separation of variables gives

\[ \hat{g} = \frac{1}{\kappa^2 \left( 1 + \frac{k_y^2}{\kappa^2} + i\omega \tau \right)} \frac{\partial^2 \hat{g}}{\partial x^2}. \quad (3.30) \]

If \( k_y \ll \kappa \), then the following simplification is valid:

\[ \hat{g} \approx \frac{1}{\kappa^2 (1 + i\omega \tau)} \frac{\partial^2 \hat{g}}{\partial x^2}. \quad (3.31) \]

The following boundary conditions can be used to solve the differential equation given by Eq. (3.31):

\[ g \bigg|_{x \to \infty} = 0, \quad (3.32) \]
\[ \frac{\partial g}{\partial x} \bigg|_{x \to \infty} = 0, \quad \text{and} \]
\[ \frac{\partial g}{\partial x} \bigg|_{b} = \Re \left\{ -\frac{z_1 e n^\infty}{kT} \frac{\partial \hat{v}}{\partial x} \bigg|_{b} \exp \left( i (\omega t - k_y y) \right) \right\}. \quad (3.34) \]

Eqs. (3.32) and (3.33) follow from the electroneutrality of the bulk solution. Eq. (3.34) follows from the imperviousness of the dielectric surface to ions and results from applying the following to Eq. (3.11):

\[ n \cdot f_j \bigg|_{b} = 0. \quad (3.35) \]
Using the boundary conditions given by Eqs. (3.32)-(3.34), the solution to Eq. (3.31) is

\[ \hat{g} = \frac{z_1 e^{i\infty} \exp \left( -\kappa x \sqrt{1 + i\omega \tau} \right)}{kT \kappa \sqrt{1 + i\omega \tau}} \frac{\partial \psi}{\partial x} \bigg|_b. \] (3.36)

### 3.4.3 Frequency-dependent potential distribution in the electrolyte

It will prove useful to state \( g \) in terms of \( \psi_b \) by finding a relation between \( \psi_b \) and \( \partial \psi_b/\partial x \). We can do this by examining Poisson's equation, Eq. (3.13):

\[ \nabla^2 \psi = \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} = -\frac{2z_1e}{\varepsilon} g. \] (3.37)

As the frequency increases, Eq. (3.37) reduces to Laplace's equation, Eq. (3.14). Melcher [Melcher81a] describes a method to solve frequency-dependent equations of this sort that are required to simultaneously satisfy both Poisson's and Laplace's equations, by considering the potential to be the sum of a particular solution, \( \varphi \), that satisfies Poisson's equation and a homogeneous solution, \( \phi \), that satisfies Laplace's equation:

\[ \psi(x, y, t) = \varphi(x, y, t) + \phi(x, y, t). \] (3.38)

Using Melcher's solution to Laplace's equation in a charge-free layer [Melcher81b] with the boundary condition that \( \phi_b \) is the complex amplitude of the potential in the \( b \) plane and the potential decays to zero at infinity, \( \phi \) can be shown to be of the form:

\[ \phi(x, y, t) = \Re \left\{ \phi_b \exp \left( i (\omega t - k_y y) - k_y x \right) \right\}. \] (3.39)

It is a reasonable assumption that the exponential decay of \( \varphi \) takes the same form as the exponential decay of \( g \) so that \( \varphi \) is given by Eq. (3.36):

\[ \varphi(x, y, t) = \Re \left\{ \phi_b \exp \left( i (\omega t - k_y y) - \kappa x \sqrt{1 + i\omega \tau} \right) \right\}, \] (3.40)
3.4 High-Frequency Model

where $\hat{\varphi}_b$ is the complex amplitude of $\varphi$ in the $b$ plane.

Using Eqs. (3.36)-(3.40) it is elementary to state $\hat{\psi}$ in terms of $\hat{\psi}_b$:

$$
\hat{\psi} = \hat{\psi}_b \frac{\exp\left(-\kappa x \sqrt{1 + i \omega \tau}\right) + \frac{i \omega \tau \exp(-k_y x)}{k_y}}{\frac{1}{\kappa \sqrt{1 + i \omega \tau}} + \frac{i \omega \tau}{k_y}}, 
$$

(3.41)

and $\partial \hat{\psi}_b / \partial x$ in terms of $\hat{\psi}_b$,

$$
\frac{\partial \hat{\psi}_b}{\partial x} = -\hat{\psi}_b \frac{1 + i \omega \tau}{\frac{1}{\kappa \sqrt{1 + i \omega \tau}} + \frac{i \omega \tau}{k_y}}.
$$

(3.42)

Thus, $\hat{g}$ takes the form:

$$
\hat{g} = -n^\infty \hat{\psi}_b \sqrt{1 + i \omega \tau} \exp\left(-\kappa x \sqrt{1 + i \omega \tau}\right) \frac{1}{\frac{1}{\kappa \sqrt{1 + i \omega \tau}} + \frac{i \omega \tau}{k_y}}.
$$

(3.43)

### 3.4.4 Boundary condition between insulating layer and electrolyte

We can relate $\hat{\psi}_b$ to the potential applied to the electrodes, $\hat{\psi}_a$, by considering the boundary conditions at the interface between the insulating layer and the electrolyte. From Gauss's law it can be shown that the $D$ field above and below the interface, denoted by $D_+$ and $D_-$ respectively, are equal if there are no real charges on the interface [DUKHIN74, TRUKHAN63]:

$$
0 = n \cdot (D_- - D_+) = n \cdot (\varepsilon_1 E_+ - \varepsilon_2 E_+),
$$

(3.44)

where $\varepsilon_1$ is the dielectric constant of the insulating layer and $E = -\nabla \psi$. If $k_y t_{\text{ins}} \ll 1$, where $t_{\text{ins}}$ is the thickness of the insulating layer, then the component of the electric field in the $x$ direction is constant throughout the insulating layer and is equal to the potential difference across the layer divided by $t_{\text{ins}}$ [MELCHER81B]. From Eq. (3.42) and the continuity of $\psi_b$ across the interface, Eq. (3.44) reduces to

$$
\frac{\varepsilon_2 (1 + i \omega \tau) \hat{\psi}_b}{\frac{1}{\kappa \sqrt{1 + i \omega \tau}} + \frac{i \omega \tau}{k_y}} = \frac{\varepsilon_1 (\hat{\psi}_a - \hat{\psi}_b)}{t_{\text{ins}}}.
$$

(3.45)
By separation of variables, we can relate $\psi_b$ to $\psi_a$:

$$\psi_b = \psi_a \frac{1}{\kappa \sqrt{1 + i \omega \tau}} + \frac{i \omega \tau}{k_y} + \frac{\tan \varepsilon_2}{\varepsilon_1} (1 + i \omega \tau).$$

(3.46)

This enables us to restate Eqs. (3.41) and (3.43) in terms of $\psi_a$:

$$\hat{\psi} = \psi_a \frac{\exp(-\kappa \sqrt{1 + i \omega \tau})}{\kappa \sqrt{1 + i \omega \tau}} + \frac{i \omega \tau \exp(-k_y x)}{k_y}$$

and

$$\hat{g} = -\psi_a \frac{n \varepsilon_2 \varepsilon_3 \varepsilon_0}{\kappa k_T} \sqrt{1 + i \omega \tau} \exp(-\kappa \sqrt{1 + i \omega \tau})$$

(3.47)

(3.48)

### 3.4.5 Electro-osmotic slip velocity

We can evaluate the slip velocity by integrating Eq. (3.17) twice with respect to $x$. Fig. 3.3 illustrates the boundary conditions for this integral: firstly, the no slip boundary condition, that the fluid velocity at the dielectric surface is constrained to be zero, and secondly, that the fluid velocity at a distance many times the Debye length from the dielectric surface reaches a constant slip velocity $v_{\text{slip}}$, so that $v_{\text{slip}}$ is given by

$$v_{\text{slip}} = \frac{2 z_1 e}{\eta} \int_0^\Delta \int_0^\Delta \left( \frac{\partial p}{\partial y} - g \frac{\partial \psi}{\partial y} \right) dx \, dx,$$

(3.49)

where $\Delta$ is a distance normal to the dielectric interface at which the charge separation due to the electric double layer becomes negligible and at which the fluid velocity is $v_{\text{slip}}$. Thus by inserting the first derivative of Eq. (3.1) with regard to $y$ and Eqs. (3.47) and (3.48) into Eq. (3.49) and allowing $\Delta$ to approach infinity (so that we include all the charge contained in the electric double layer) and performing the double integration we can show that the time-averaged slip velocity $\langle v_{\text{slip}} \rangle$ is given by

$$\langle v_{\text{slip}} \rangle = \frac{\varepsilon_2 |\psi_a|^2 \omega \tau}{2 \eta k \varepsilon_1} \left| \frac{1}{\kappa \sqrt{1 + i \omega \tau}} + \frac{i \omega \tau}{k_y} + \frac{\tan \varepsilon_2}{\varepsilon_1} (1 + i \omega \tau) \right|^2,$$

(3.50)
where a complex quantity surrounded by straight brackets denotes the absolute value of the complex quantity and we have neglected some terms that are insignificant because $k_y \ll \kappa$ and the time-average of $\partial p/\partial y$ is zero. For traveling wave potentials, the time average of Eq. (3.19) is zero and it does not affect the time-averaged electro-osmotic slip velocity.

Eq. (3.50) can be shown to be compatible with an equation derived for similar conditions by Ehrlich and Melcher [EHRLICH82] by replacing $|\hat{\psi}_a|$ with $|\partial \hat{\psi}_b/\partial x|$ by means of Eqs. (3.42) and (3.46). Eq. (3.50) has the advantage that the slip velocity can be related much more easily to experimental results because it is more practical to hold the excitation voltage applied to the electrodes constant. This equation shows that the slip velocity tends to zero at frequencies much higher or lower than the double layer relaxation frequency as was shown by our experiments. The frequency dependence of slip velocity is more complicated than that derived by Ehrlich and Melcher [EHRLICH82], being dependent on the Debye length, propagation constant, thickness of the insulating layer and the dielectric constant of the insulating layer and fluid, in addition to the relaxation time and frequency. The electro-osmotic slip velocity is proportional to the square of the excitation potential as shown experimentally in Fig. 2.4. The slip velocity is proportional to the Debye length, this means the slip velocity is inversely proportional to the square root of the concentration of the electrolyte.

In Fig. 3.4, three graphs are plotted that show how this type of streaming can be optimized. Fig. 3.4(a) shows how the slip velocity increases as the wavelength of the traveling-wave electrode array decreases while the frequency of maximum slip velocity shifts to higher frequencies. Fig. 3.4(b) shows how the slip velocity increases as the factor $t_{ins} \varepsilon_2/\varepsilon_1$ decreases while the frequency of maximum slip velocity shifts very slightly to lower frequencies. Fig. 3.4(c) shows how the slip velocity increases as $\kappa^{-1}$ increases. These graphs show that the miniaturization of the dimensions of the setup is the most important factor enabling this form of electro-osmotic flow to take place over the traveling-wave spiral. The slip velocity increases as dimensions associated with the experimen-
Fig. 3.3: The slip velocity increases from a value of zero at the dielectric surface to a value of $v_{slip}$ at the edge of the double layer.

tal setup, the wavelength of the traveling-wave electrode structure and the thickness of the insulating layer decrease. Significantly the slip velocity is dependent on the Debye length, this means that at high salt concentrations (i.e. high conductivity) the slip velocity decreases. If the dimensions are too large, the streaming will be of too low velocity for the force on the latex beads to overcome Brownian motion, at least within the terms of validity of our model. The term relating to the thickness of the insulating layer is coupled to the ratio of the dielectric constant of the medium to that of the insulating layer itself. Thus thin layers of high dielectric constant material are the best material choice to optimize this type of electro-osmotic transport.

3.4.6 Linearity Conditions

In addition to the condition that $k_y \ll \kappa$ there are two other significant linearity conditions for these theoretical models: the surface potential condition ($kT/ze$) and the surface conductivity condition (the Dukhin number). The surface potential can be divided into two components: the electrokinetic potential of the insulator surface $\zeta$ and the potential due to the ac excitation.
3.4 High-Frequency Model

Fig. 3.4: Frequency dependence of electro-osmotic slip velocity as given by Eq. (3.50) using the following data: $\eta = 10^{-3}$ Ns/m$^2$, $\varepsilon_1 = 2.0\varepsilon_0$, $\varepsilon_2 = 80\varepsilon_0$, and $|\psi_0| = 250$ mV. (a) Slip velocity increases as the wavelength of the traveling-wave decreases when $t_{in}\varepsilon_2/\varepsilon_1 = 2$ $\mu$m and $\kappa^{-1} = 25$ nm. (b) Slip velocity increases as the factor $t_{in}\varepsilon_2/\varepsilon_1$ decreases when $\lambda = 6$ $\mu$m and $\kappa^{-1} = 25$ nm. (c) Slip velocity increases as the Debye length increases when $\lambda = 6$ $\mu$m and $t_{in}\varepsilon_2/\varepsilon_1 = 2$ $\mu$m.
Electrokinetic potential

The electrokinetic potential is the equilibrium potential at the shear plane of the surface in the absence of a potential applied to the electrodes. For our experimental conditions, the electrokinetic potential of the HFP surface can be estimated from data describing Teflon surfaces from Kirby and Hasselbrink [KIRBY2004], that is, between $-50$ and $-70$ mV. This means that in our experiments the application of the traveling wave signal acts to perturb the equilibrium electric double layer while in our model the traveling wave is solely responsible for double layer formation. Nevertheless the electrokinetic equations are not generally tractable analytically and the assumption of low potential makes an analytical solution possible and the treatment illustrates many of important factors that affect the phenomenon. Furthermore the time-average of the product of the constant part of the double layer charge with the tangential field (alternating) is zero. The presence of this equilibrium electrokinetic potential probably acts to attenuate the electro-osmotic velocity.

Applied Potential

In most colloid and interface science textbooks, it is stated that the Debye-Hückel approximation is limited to electrokinetic potentials less than $kT/ze$ [HUNTER2001, LYKLEMA95] or approximately 25 mV for univalent ions. Although counterintuitive, applying potentials of the order of 500 mV does not necessarily invalidate the linearity condition if the electrodes are insulated. The $kT/ze$ limit is due to the linearization of the complete Poisson-Boltzmann equation. At higher potentials, the non-linear complete solution to the Poisson-Boltzmann equation is valid.

At very low frequency, e.g. $\omega = 0$, Eq. (3.41) agrees with the solution of the linearized Poisson-Boltzmann equation, that $\psi = \psi_0 \exp(-kx)$ which is a direct consequence of our simplification of the perturbation to the ion densities to sinusoidal form. In moving from Eq. (3.26) to Eq. (3.27), we state that the substitute variable $h$ is negli-
gible if $g < n^\infty$. In effect this condition is the origin of the $kT/ze$ limit, if the perturbation to the concentration of positive and negative ions in the double layer is equal and opposite, linearization is valid. Only the component of the potential that is linearly related to the electric double layer charge is of significance, this is the potential drop across the double layer.

To understand how the applied potentials do not invalidate the linearity condition, it helps to recall how the potential is divided into two components in Eq. (3.38). Eq. (3.41) can be split into these two components:

$$
\varphi(x, y, t) = \Re \left\{ \frac{\hat{\psi}_a \exp(i(\omega t - k_y y) - k_x \sqrt{1 + i\omega \tau})}{\frac{1}{\kappa \sqrt{1 + i\omega \tau}} + \frac{i \omega \tau}{k_y} + \frac{1}{\varepsilon_1}} \right\} \quad \text{and} \quad (3.51)
$$

$$
\phi(x, y, t) = \Re \left\{ \frac{\hat{\psi}_a \exp(i(\omega t - k_y y) - k_y x)}{\frac{1}{\kappa \sqrt{1 + i\omega \tau}} + \frac{i \omega \tau}{k_y} + \frac{1}{\varepsilon_1}} \right\}. \quad (3.52)
$$

The first component $\varphi$ satisfies Poisson's equation and can be related to the charge density in the double layer and its amplitude reduces with increasing frequency. The second component $\phi$ satisfies Laplace's equation and its amplitude increases from zero at low frequencies to a value much greater than $\varphi$ at even relatively low frequencies. If $k_y \ll \kappa$, $\phi$ can be considered constant across the double layer so that $|\varphi_b|$ corresponds to the potential dropped across the double layer. Fig. 3.5 shows how $|\varphi_b|$ decreases with increasing frequency and is always less than 10 mV for our experimental conditions.

**Surface Conductivity**

The electrical conductivity is directly related to the ionic concentration. The formation of the double layer can result in a local perturbation to the ionic concentration so that the conductivity in the region of the electric double layer differs from that of the bulk fluid. This deviation is referred to as surface conductivity [LYKLEMA95, BIKERMAN33, DUKHIN73].
The Dukhin number $Du$ is the ratio of surface conductivity to bulk conductivity and is given by

$$Du \approx \frac{1/\kappa}{L_c} \left( \cosh \left( \frac{V z e}{2 k T} \right) - 1 \right), \quad (3.53)$$

where $V$ is the potential drop across the double layer. Surface conductivity effects will invalidate both of the models described above if the Dukhin number is not much less than one. Bazant et al. show how exceeding a limit similar to $Du$ leads to strongly non-linear behaviour, that is, to bulk concentration gradients and, at very high voltages, transient space charge [BAZANT2004].

The Dukhin number is much less than one for our experimental conditions. For surface conductivity to influence ac electro-osmotic flow, one might expect the frequency of maximum slip velocity to be greater than that predicted by the models, in much the same way as surface conductivity affects dielectrophoresis [HUGHES99].
3.5 Comparison of Models

Eqs. (3.9) and (3.50) have a similar form and exhibit primary dependence on the term $\varepsilon_2 |\hat{v}_a|^2 \omega \tau / (2 \eta k)$. The difference between the two expressions is that Eq. (3.50) contains the term $1 + i\omega \tau$ three times. Two of these cases account for the relaxation of the double layer and the third is significant because the capacitance of the insulating layer doesn’t relax at high frequencies.

Fig. 3.6 shows how the two models converge when the wavelength of the structure is long. Eq. (3.5) shows that $\omega_c$ is inversely proportional to wavelength, so that longer wavelengths lead to $\omega_c$ values that are much less than the double layer relaxation frequency. Fig. 3.7 shows how the two models converge as the dielectric constant of the insulation layer increases, this is equivalent to increasing the capacitance of the insulating layer so that the capacitance of the double layer predominates, so that $\delta < 1$. It is also possible to decrease the thickness of the insulating layer to similar effect. The two models converge when $\omega_c \tau \ll 1$, where $\omega_c$ is given by Eq. (3.5), because the extra terms included in Eq. (3.50) disappear. If the condition $\omega_c \tau \ll 1$ is not fulfilled, the first model becomes invalid and it is more correct to use the second model. The relaxation frequency of the second model never exceeds the double layer relaxation frequency.

3.6 Discussion

3.6.1 Comparison of Experiment with Theory

Eqs. (3.9) and (3.50) predict fluid flow in the same direction as was observed experimentally. This rules out the possibility that the fluid flow is caused by traveling-wave induced electroconvection [FUHR94, FUHR92, GIMSA97, MÜLLER93]. Traveling-wave dielectrophoresis [JONES95] would cause bead motion in the same direction but this possibility may be discounted because a dielectrophoretic relaxation was observed for
Fig. 3.6: Frequency dependence of the two models for the electro-osmotic slip velocity as given by Eqs. (3.9) and (3.50) using the following data: \( \eta = 10^{-3} \) Ns/m\(^2\), \( \varepsilon_1 = 2.0 \varepsilon_0 \), \( \varepsilon_2 = 80 \varepsilon_0 \), \( |\psi_0| = 250 \) mV, \( t_{thin} \varepsilon_2 / \varepsilon_1 = 2 \) \( \mu \)m, and \( \kappa^{-1} = 25 \) nm. (a), (b), and (c) show how the two models converge as the wavelength increases from 6 \( \mu \)m to 60 \( \mu \)m and 600 \( \mu \)m respectively.
Fig. 3.7: Frequency dependence of the two models for the electro-osmotic slip velocity as given by Eqs. (3.9) and (3.50) using the following data: \( \eta = 10^{-3} \) Ns/m², \( \lambda = 6 \mu m \), \( \varepsilon_2 = 80 \varepsilon_0 \), \( |\psi_0| = 250 \) mV, \( t_{\text{inj}} \varepsilon_2/\varepsilon_1 = 2 \mu m \), and \( \kappa^{-1} = 25 \) nm. (a), (b), and (c) show how the two models converge as \( \varepsilon_1 \) increases from \( 2 \varepsilon_0 \) to \( 15 \varepsilon_0 \) and \( 80 \varepsilon_0 \) respectively.

AC Electro-osmotic Pumping for Microfluidic Systems
frequencies of the order of 5 MHz for the prepared latex bead disper-
sions, that is, for frequencies lower than 5 MHz beads were attracted to
the electrodes and at higher frequencies they were repelled from the elec-
trodes. This is consistent with the work of Hughes et al. [HUGHES99]
who observed a dielectrophoretic relaxation at similar frequencies for
carboxylate latex beads in aqueous electrolytes of the same conductivity
range. Traveling-wave dielectrophoresis takes place at frequencies in the
range of a dielectrophoretic relaxation [JONES95].

We only compare the experimental results with the second model,
as \( \omega_c \) is greater than the double layer relaxation frequency. This is be-
cause of (i) the small width of electron-beam-microfabricated electrodes
and (ii) the factor \( \delta \) is much greater than one because the thickness of
the insulating layer is of the same order of the Debye length while its
dielectric constant is much lower than that of water. Fig. 3.8 (a) shows
the experimental data for the observed velocity of the fluorescent latex
beads for each of the three electrolytic solutions for an applied potential
of 450 mV amplitude as a function of frequency. These data were pre-
viously presented in Fig. 2.3. This shows how for the identical applied
potential and increasing electrolyte conductivity the velocity decreases
and the frequency of peak velocity shifts to higher frequencies.

There are some significant differences between theory and experi-
ment. The experimentally observed velocity is significantly less than the
predicted value. The decrease of velocity with increasing electrolyte con-
ductivity is not as predicted by Eq. (3.50) although it does decrease with
increasing conductivity. We concur with the observation of Brown et al.
[BROWN2001] that the observed velocity varies over the lifetime of the
electrode structure. González et al. [GONZÁLEZ2000] also noted that
the velocity predicted by theory was higher than that measured experi-
mentally. The deviations observed in our experiments are probably due
to the equilibrium electrokinetic potential of the surface being not only
non-zero but greater than \( kT/ze \) so that the linearization is not fulfilled.
In section 3.4.6, we note how the electrokinetic potential in the absence
of an applied potential dominates the formation of the double layer at
3.6 Discussion

Fig. 3.8: (a) Experimentally measured values of the velocity of the fluorescent latex beads plotted against frequency at an applied potential of 450 mV at three different medium conductivities: 2.0 mS/m (▼), 4.19 mS/m (■) and 8.36 mS/m (●), that is, Debye lengths of 26.3 nm, 18.1 nm, and 12.8 nm respectively. The dotted line is fitted to the experimental data. The behaviour predicted Eq. (3.50) is shown by the continuous lines. The square wave of 450 mV amplitude is represented by the first harmonic of the Fourier series. (b) The same data normalized to the peak value measured and plotted against the radial frequency multiplied by the double layer relaxation time. The line fitted to the experimental data points is from Eq. (3.50).
all frequencies and that the applied potential merely acts to perturb the electrokinetic potential. It is likely that the dependence of velocity on conductivity is linked to the dependence of the electrokinetic potential on conductivity in a way that is not taken into account by Eq. (3.50).

Fig. 3.8 (b) makes use of the same data as Fig. 3.8 (a) but the velocity is normalized to the peak value for each curve and the angular frequency, $\omega$, is normalized by multiplication with the double layer relaxation time, $\tau$. The data is fitted to Eq. (3.50), the normalization of both frequency and velocity leads to a curve that is largely independent of medium conductivity, if $k_y \ll \kappa$. It is clear that while the theory does not perfectly model our results that the form of the predicted curve is similar to the experimental results and that the frequency of the peak velocity is lower than but of the same order as that predicted. It is also clear that while there is some scatter in the frequency of peak velocity and that the conductivity range examined is not very large that the variation of the frequency of peak velocity with electrolyte conductivity is roughly that predicted by Eq. (3.50).

Fig. 2.3 shows how the frequency of peak velocity is independent of applied potential; at least for the low applied potentials used in this study and presumed by our model. Eq. (3.50) relates the slip velocity to the Debye length and consequently to the inverse of the square root of conductivity. Fig. 2.4 shows that the experimentally observed velocity confirms the prediction of Eq. (3.50) that the electro-osmotic slip velocity is proportional to the square of the applied potential. That we have observed this proportionality can be used to support the validity of the model on the basis of the low potentials applied to the electrodes.

3.6.2 Deviations of Experimental Setup from Theoretical Model

It must be noted that the experimental set-up implemented is more complicated than the theoretical model used to describe the system but that it is a suitable prototype to demonstrate the principle of traveling-
3.6 Discussion

wave induced electro-osmotic flow.

Firstly, we chose to conduct our experiments using a spiral electrode structure and then chose to simulate a linear electrode structure. This point is mitigated by the fact that all of the relevant dimensions, for example of the radius of curvature of the spiral structure are much larger than the Debye length, so that on the scale of the Debye length the radius of curvature of the spiral appears to be flat. Also, recirculation due to the form of the spiral electrode restricts the desired flow to within a couple of microns of the electrodes. In chapter 5, we show how the microfabrication of a linear structure allows flow to be generated at greater distances.

Secondly, we presume an idealized traveling wave that is a pure sinusoid both in the plane of the electrodes and in the plane of the interface between the insulating layer and the fluid. In practice, the application of a four-phase square wave signal to an electrode structure leads to a distorted traveling wave that is neither spatially or temporally identical to the ideal traveling wave. Also, the electrodes are not infinitely thin, they are 80 nm thick, indeed they are thicker than both the insulating layer (50 nm) and the Debye length (< 27 nm). This thickness could act to attenuate the flow by acting as a surface roughness, surface roughness acts to reduce the velocity of electrokinetic flows [Hu2003]. Furthermore, field enhancement occurs at the edge of an electrode that may lead to further distortion of the traveling-wave signal.

Thirdly, we trace the movement of latex beads in order to ascertain the fluid velocity, the electric field is distorted by the presence of the beads and the beads themselves may be affected by dielectrophoresis [Jones95]. At higher applied potentials the beads are attracted towards the electrodes by positive dielectrophoresis and their transport by fluid motion ceases.

Finally, we simplify the nature of the dielectric interface by neglecting the influence of the Stern layer and the zeta potential of the surface [Kirby2004]. In this case, the Stern layer capacitance is in se-
ries with the capacitance of the insulating layer and should be negligible but we estimate that the electrokinetic potential of the teflon-like surface is around twice $kT/ze$. The theoretical approach presented in this chapter is simplified to an extent but captures the qualitative trends of the experimental results and is sufficient to explain the core concepts at the heart of the phenomenon.

Eq. (3.50) proves useful in describing the important factors on which this form of electro-osmosis depends and in demonstrating that fluid flow of this kind can take place for low applied potentials and the experimental results show that many of the most important factors, such as, the frequency profile of slip velocity, the frequency of maximum velocity and the proportionality of the velocity to the square of the applied potential agree well with Eq. (3.50). It offers insight into how electro-osmotic flow can be optimized.
Chapter 4

Flow Profile over Traveling Wave Electrodes

The analytical simulations presented in chapter 3 neglected the exact geometry of the electrodes by presuming that an idealised traveling wave of potential exists at an interface. In our experiments, we used four electrodes to generate this traveling wave of potential. Due to the discrete nature of these electrodes it is to be expected that the potential above the electrodes deviates from the traveling wave described in the simulation. To examine this problem, we choose to follow the example of Ramos et al. [RAMOS2003] who described ac electro-osmotic pumping above asymmetric electrode pairs using the charge simulation method. A numerical method is in some ways more suited to dealing with arbitrary
4 Flow Profile over Traveling Wave Electrodes

electrode geometry than the analytical approach described in chapter 3.

The solution is divided into two parts. In the first, we solve for the potential drop across the double layer by numerically computing the potential on the edge of the double layer by the charge simulation method. Once this potential is known, the electro-osmotic slip velocity can be calculated. In the second part, the electro-osmotic slip velocity is used as a boundary condition to simulate the fluid flow in the bulk fluid.

4.1 Basic model and governing equations

![Diagram of electrode geometry](image)

Fig. 4.1: Schematic diagram of the electrode geometry modeled in the numerical simulation. The electrodes all have the same widths and the electrode gaps have the same value. The origin is in the plane just outside the electric double layer so that the plane where \( y = 0 \) is indicated by the dashed line.

Fig. 4.1 shows the traveling wave electrode system to be modeled, a four-phase traveling wave electrode system. The electrode widths and gaps are equal. Traveling wave signals of the form used experimentally are applied to the four electrodes. Electrical signals are applied to the electrodes in Fig. 4.1 so that a traveling wave of potential can be approximated above the electrode structure. The potential of each electrode \( V_j \) is of sinusoidal form, \( V_j = \Re [V_0 \exp (i (\omega t \pm j \pi/2))] \) where \( V_0 \) is the amplitude of the signals applied to the electrodes and \( j \) is the number of the electrode as indicated in Fig. 4.1 and \( \pm \) is positive or negative depending on the direction of travel of the traveling wave. There is a 90° phase difference between the signals applied to neighbouring electrodes.

The potential \( \Phi \) is the potential just outside the electric double
4.1 Basic model and governing equations

layer. Outside the electric double layer in the bulk fluid the potential distribution is described the Laplace equation:

\[ \nabla \Phi = 0 \quad (4.1) \]

This model is valid for the conditions of low frequency so that the frequency is much lower than the double layer relaxation frequency. Therefore the electric double layer can be described by a simple capacitor \( C_{edl} = \varepsilon \kappa \) where \( \varepsilon \) is the dielectric constant fluid \( \kappa^2 = \sigma / \varepsilon D \), \( \sigma \) is the conductivity of the fluid and \( D \) is the diffusion constant of the ions in solution. Ohm's law describes ion transport in the bulk solution:

\[ \frac{\partial \sigma_D}{\partial t} = \sigma n \cdot E. \quad (4.2) \]

where \( \sigma_D \) is the surface charge density associated with the electric double layer.

Relating the surface charge to the surface capacitance gives the boundary condition for the normal electric field above an electrode:

\[ \sigma \frac{\partial \Phi}{\partial y} = i \omega C_{edl} (\Phi - V_j) \quad (4.3) \]

To obtain the boundary condition for the potential at the interface between the bare substrate and the liquid, we can examine Gauss's law. The displacement field is continuous across the interface, thus;

\[ (\sigma + i \varepsilon \omega) \frac{\partial \Phi}{\partial y} = (\sigma_s + i \varepsilon_s \omega) \frac{\partial \Phi_s}{\partial y} \quad (4.4) \]

where \( \sigma_s, \varepsilon_s \) and \( \Phi_s \) are the conductivity, dielectric constant and the potential in the substrate respectively. If the conductivity of the substrate is much less than that of the fluid and the frequency is much less than the double layer relaxation frequency, \( \omega \ll \sigma / \varepsilon < \sigma / \varepsilon_s \) then the normal derivative of the potential above the gaps between the electrodes can be considered negligible:

\[ \frac{\partial \Phi}{\partial y} = 0 \quad (4.5) \]
If the wavelength of the traveling wave is much larger than the Debye length then the tangential current can be neglected. The necessity that the normal current at the edge of the electric double layer integrated over a wavelength of the traveling wave electrode structure is zero gives a further boundary condition:

\[
\frac{1}{L/2} \int_{-L/2}^{L/2} \frac{\partial \Phi}{\partial y} \, dx = 0
\]  

(4.6)

The Smoluchowski equation relates the electro-osmotic slip velocity, \( u \), to the tangential electric field, \( E_t \), the dielectric constant of the fluid, \( \varepsilon \), the viscosity of the fluid, \( \eta \), and the potential drop across the double layer, \( \Delta \Phi = \Phi - \Phi_0 \):

\[
u = \frac{\varepsilon \Delta \Phi}{\eta} E_t
\]  

(4.7)

The time-averaged slip velocity is given by [González2000, Green2002, Ramos2003]:

\[
\langle u_{\text{slip}} \rangle = -\frac{\varepsilon}{4\eta} \frac{\partial}{\partial x} \left[ |\Phi - V_j|^2 \right],
\]  

(4.8)

For an incompressible fluid of uniform mass density and viscosity, fluid flow is governed by the incompressible Navier-Stokes equations:

\[
\eta \nabla^2 u - \nabla p = 0, \quad \nabla \cdot u = 0
\]  

(4.9)

For net flow to take place it is necessary that the integral of the slip velocity over one wavelength is non-zero:

\[
U = \frac{1}{L} \int_{-L/2}^{L/2} u \, dx \neq 0
\]  

(4.10)

where \( U \) is the average slip velocity.
4.2 Numerical Solution of the Potential Distribution

To simplify numerical simulation, all distances in this model are normalised by dividing by the width of the electrodes, \( L/8 \). The normalised frequency \( \Omega \) is obtained from Eq. 4.3:

\[
\Omega = \omega k \tau L/8 \quad (4.11)
\]

4.2 Numerical Solution of the Potential Distribution

In this section, we will determine the potential at the interface between the electric double layer and the bulk fluid by the charge density method. The charge density method employs the relationship between the charge density located at discrete electrode elements and the potential fields that arise from these elements [BEATOVIČ92]. By the principle of superposition, the potential at a particular point is the summation of the potential due to each discrete charge element.

The fundamental solution for the potential \( \phi_u(x, y) \) due to a uniform grid of source lines of unit charge is given by [MORSE53]:

\[
\phi_u(x, y) = -\frac{1}{4\pi \varepsilon} \ln \left[ \sinh^2 \left( \frac{ky}{2} \right) + \sin^2 \left( \frac{kx}{2} \right) \right] \quad (4.12)
\]

The solution for every charge element can be superimposed so that the superposition describes the electrode geometry. This superposition in combination with the sum of the charge distribution in the electric double layer \( \sigma_D(x) \) and on the electrodes \( \sigma_E(x) \) is \( \sigma_{Tot}(x) = \sigma_D(x) + \sigma_E(x) \):

\[
\Phi(x, y) = \int_{-L/2}^{L/2} \sigma_{Tot}(x') \phi_u(x - x', y) \, dx' \quad (4.13)
\]

The surface charge can be related to normal derivative of the potential at the edge of the double layer through \( \sigma_{Tot}(x) = \)
56 4 Flow Profile over Traveling Wave Electrodes

\(-2\varepsilon\partial\Phi(x,0)/\partial y, \) so that for \(y > 0:\)

\[
\Phi(x, y) = \frac{1}{2\pi} \int_{-L/2}^{L/2} \Phi_y(x',0) \ln \left[\sinh^2(ky/2) + \sin^2(kx/2)\right] dx'
\]  

(4.14)

where \(\Phi_y(x, 0) = \partial\Phi(x, 0)/\partial y.\) The Green's function \(G\) is thus:

\[
G(x - x', y) = \frac{1}{2\pi} \ln \left[\sinh^2(ky/2) + \sin^2(kx/2)\right]
\]  

(4.15)

Putting \(y = 0\) gives an equation that can be used as the basis of the boundary solution:

\[
\Phi(x, 0) = \frac{1}{2\pi} \int_{-L/2}^{L/2} \Phi_y(x', 0) \ln \left[\sin^2(kx/2)\right] dx'
\]  

(4.16)

This gives four simultaneous equations for \(\Phi_y(x, 0)\) above each of the four electrodes:

\[
V_1 + \frac{1}{i\Omega} \Phi_y(x, 0) = \int_{-L/2}^{L/2} \Phi_y(x', 0) G(x - x', 0) dx' \quad \text{for } x_1 < x < x_2
\]  

(4.17)

\[
V_2 + \frac{1}{i\Omega} \Phi_y(x, 0) = \int_{-L/2}^{L/2} \Phi_y(x', 0) G(x - x', 0) dx' \quad \text{for } x_3 < x < x_4
\]  

(4.18)

\[
V_3 + \frac{1}{i\Omega} \Phi_y(x, 0) = \int_{-L/2}^{L/2} \Phi_y(x', 0) G(x - x', 0) dx' \quad \text{for } x_5 < x < x_6
\]  

(4.19)

\[
V_4 + \frac{1}{i\Omega} \Phi_y(x, 0) = \int_{-L/2}^{L/2} \Phi_y(x', 0) G(x - x', 0) dx' \quad \text{for } x_7 < x < x_8
\]  

(4.20)

4.2.1 Electrical Solution

In the following section, the system of simultaneous equations described in Eqs. (4.17-4.20) is solved by dividing the boundary into \(N\) discrete

AC Electro-osmotic Pumping for Microfluidic Systems
sections. Over each section the potential can be considered to be constant so that the integration can be performed over this element alone. The equations can be solved by testing the system at each of these \( N \) discrete sections resulting in a system of \( N \) simultaneous equations. Additionally it is necessary to take Eq. (4.6) into account so that we have a system of \( N+1 \) equations in \( N \) variables. This system of simultaneous equations is overdetermined and can be solved in Matlab using the least squares method.

Fig. 4.2: Four graphs showing respectively (a) the absolute potential \(|\Phi|\), (b) the phase angle of \( \Phi \), (c) the real part of the potential \( \Phi \) and (d) the electric double layer charge \( \sigma_D \) plotted against \( x \). In (b), (c), and (d), curves are displayed for each of the electrodes numbered 1-4 for \( \omega t = 25^\circ \). In (a) the curve is identical above all electrodes and is independent of applied phase. In all graphs \( \Omega = 1 \) and the traveling wave moves from right to left. All quantities are normalised so that the units are dimensionless.

Fig. 4.2 shows the value of the following quantities at \( y = 0 \) above each electrode: absolute potential, the phase and the real part of the
potential for $\omega t = 25^\circ$. In Fig. 4.2 (a), the absolute part of the potential varies in exactly the same way above each of the electrodes. Fig. 4.2 (b) shows how the phase above each electrode is shifted by $90^\circ$ which is exactly the same as the phase difference between the signals applied to the electrodes. Fig. 4.2 (c) shows the real part of the potential for $\omega t = 25^\circ$. The significance of the real part of the potential is that for electrodes 2 and 4 the gradient of the potential across the electrodes is not consistently in the same direction but for electrodes 1 and 3 the gradient is consistently in one direction. Fig. 4.2 (d) shows the electric double layer charge above each electrode for $\omega t = 25^\circ$. The magnitude of the double layer charge above electrodes 2 and 4 is lower than that above electrodes 1 and 3. The gradient of the potential above electrodes 2 and 4 leads to fluid flow in the same direction. In this way, as the traveling wave moves across the electrodes, at any one time the instantaneous flow caused may be significant above any two electrodes and relatively insignificant over the other two so that the predominant direction of flow is in the direction of travel of the traveling wave.

The solution of the boundary potential can be combined with Eq. (4.8) to give the time-averaged slip velocity over the electrodes. The time-averaged slip velocity between the electrodes is zero as described by Eq. (4.5). Fig. 4.3 (a) shows the time-averaged slip velocity above the electrode surface. The maximum frequency occurs at a frequency quite close to $\Omega = 1$.

### 4.3 Profile of Fluid Flow

In this section, we will use the electro-osmotic slip velocity calculated in the preceding section as a boundary condition to determine the fluid flow in the bulk fluid.
4.3 Profile of Fluid Flow

Fig. 4.3: (a) The variation of the time-averaged electro-osmotic slip velocity as given by Eq. (4.8) as a function of position across the electrode surface. (b) The variation of the electro-osmotic slip velocity averaged over the surface \( U \) as given by Eq. (4.8) as a function of normalised frequency, \( \Omega \). The maximum velocity is close to the \( \Omega = 1 \). The traveling wave moves from right to left. All quantities are normalised so that the units are dimensionless.

4.3.1 Fourier Components of Fluid Flow

Fourier series analysis will be used to model the fluid flow. The Fourier components of the time-averaged fluid velocity and pressure are:

\[
    \begin{align*}
    u &= \sum_{n=-\infty}^{\infty} u_n(y) \exp(ik_nx), \\
    v &= \sum_{n=-\infty}^{\infty} v_n(y) \exp(ik_nx), \\
    p &= \sum_{n=-\infty}^{\infty} p_n(y) \exp(ik_nx), \\
    \end{align*}
\]

(4.21)

where \( k_n = nk = 2n\pi/L \), \( n \) is an integer, the fluid velocity vector \( \mathbf{u} \) is defined by \( \mathbf{u} = u \mathbf{e}_x + v \mathbf{e}_y \), and \( \mathbf{e}_x \) and \( \mathbf{e}_y \) are unit vectors in the \( x \) and \( y \) directions respectively. The Navier-Stokes equations, Eq. (4.9), require that:

\[
    ik_n u_n + \frac{\partial v_n}{\partial y} = 0 
\]

(4.22)

\[
    \eta \left( -k_n^2 u_n + \frac{\partial^2 u_n}{\partial y^2} \right) - ik_n p_n = 0 
\]

(4.23)

\[
    \eta \left( -k_n^2 v_n + \frac{\partial^2 v_n}{\partial y^2} \right) - \frac{\partial p_n}{\partial y} = 0 
\]

(4.24)
The boundary conditions at \( y = 0 \) are that the tangential velocity is equal to the electro-osmotic slip velocity and the normal velocity is zero:

\[
\begin{align*}
    u_n(0) &= \int_{-L/2}^{L/2} u(x, 0) \exp(-ik_n x) \, dx \\
    v_n(0) &= 0
\end{align*}
\]  

(4.25)  

(4.26)

The boundary conditions as \( y \to \infty \) are that the velocity in the \( x \) direction becomes constant and that the velocity in the \( y \) direction approaches zero:

\[
\begin{align*}
    \lim_{y \to \infty} \frac{\partial u_n}{\partial y} &= 0 \\
    \lim_{y \to \infty} v_n(y) &= 0
\end{align*}
\]  

(4.27)  

(4.28)

Combining the Stokes equation for the Fourier components, it can be shown that

\[
\begin{align*}
    \left( \frac{\partial^2}{\partial y^2} - k_n^2 \right)^2 u_n(y) &= 0, \\
    \left( \frac{\partial^2}{\partial y^2} - k_n^2 \right)^2 v_n(y) &= 0, \\
    \left( \frac{\partial^2}{\partial y^2} - k_n^2 \right)^2 p_n(y) &= 0
\end{align*}
\]  

(4.29)  

(4.30)  

(4.31)

The solutions of these equations that satisfy the boundary conditions is

\[
\begin{align*}
    u &= \sum_{n=-\infty}^{\infty} u_n(0)(1 - |k_n| y) \exp(-|k_n| y + ik_n x), \\
    v &= -i \sum_{n=-\infty}^{\infty} u_n(0)k_n y \exp(-|k_n| y + ik_n x), \\
    p &= -i2\eta \sum_{n=-\infty}^{\infty} u_n(0)k_n \exp(-|k_n| y + ik_n x)
\end{align*}
\]  

(4.32)  

(4.33)  

(4.34)
4.3 Profile of Fluid Flow

We can define the stream function $\Psi$:

$$
\Psi = \sum_{n=-\infty}^{\infty} u_n(0)y \exp(-|k_n|y + ik_n x)
$$

where

$$
u = \frac{\partial \Psi}{\partial y}
$$

$$
v = -\frac{\partial \Psi}{\partial x}.
$$

By inserting Eq. (4.25) into Eq. (4.35):

$$
\Psi = \frac{1}{L} \int_{-L/2}^{L/2} dx' u(x', 0) \sum_{n=-\infty}^{\infty} \exp(-|k_n|y + ik_n (x - x'))
$$

The series can be summed by considering that $\sum_{n=1}^{\infty} r^n = r/(1 - r)$ for $|r| < 1$ and $r_{\pm} = \exp(k(\pm i(x - x') - y))$, giving

$$
\Psi = \frac{1}{L} \int_{-L/2}^{L/2} dx' u(x', 0) \frac{y \sinh(k y)}{\cosh(k y) - \cos[k(x - x')]} \quad (4.39)
$$

4.3.2 Results

On inserting the solution for the time-averaged electro-osmotic slip velocity into the definition of $\Psi$ given by Eq. 4.39, it is possible to simulate the velocity profile of the fluid flow by making use of Eqs. 4.36 and 4.37.

Fig. 4.4 depicts the fluid flow profile in the form of streamlines and a vector field map. The figures show clearly that uniform directed flow takes place at distances from the surface greater than the electrode width. That the component of the velocity in the vertical direction is only of significant value close to the electrodes is a factor in causing the high standard deviations resulting from the experimental results in chapters 2 and 5.
Fig. 4.4: (a) Streamlines and (b) a vector field showing the fluid flow field above traveling wave electrodes for an applied traveling wave moving from right to left.

By adjusting the width of the electrodes and the gaps between the electrodes to differing values, we could perform simulations that predict the effect of these values on causing electro-osmotic flow. In performing these simulations, the width used for normalisation was given by \((W +\)
4.3 Profile of Fluid Flow

\( G/2 \), where \( W \) and \( G \) are respectively the width of the electrodes and the gaps between electrodes in normalised units. In Fig. 4.5(a), it can be seen that the velocity increases as the ratio of the width the electrodes to the gaps between them increases. The boundary condition given by Eq. 4.3 means that the slip velocity at positions between the electrode being zero so that electro-osmotic flow originates at the surface of the electrodes. Figs. 4.5(b) and (c) depict the fluid flow profile in the form of a vector field map for two extreme electrode width to gap ratios. For thin electrode widths, as shown in Fig. 4.5(b), the most significant component of the flow profile is the vertical part close to the electrodes. For wide electrode widths, as shown in Fig. 4.5(c), the most significant component of the fluid flow is in the lateral direction so that strong fluid flow in the desired lateral direction is predicted. Thus the efficiency of ac electro-osmotic flow can be increased by increasing the ratio of electrode width to electrode gaps. In addition, in Fig. 4.5(c), the waviness of resulting flow is considerably less than the flow in Fig. 4.5(b) or Fig. 4.4. In general, Fig. 4.5 shows that small electrodes gaps and larger electrodes lead to more efficient and regular ac electro-osmotic flow above traveling wave electrodes. The most significant factor in causing this type of flow is to decrease the overall wavelength of the electrode structure but the relation between the width of electrodes and the size of the gaps between them can not only increase the velocity of flow but also the reduce the waviness of the flow.

AC Electro-osmotic Pumping for Microfluidic Systems
Fig. 4.5: (a) The variation of average electro-osmotic slip velocity $U$ as given by Eq. (4.8) as a function of normalised frequency, $\Omega$, on variation of the ratio between electrode width and the size of the gaps between electrodes. (b) A vector field showing the fluid flow field above traveling wave electrodes for an applied traveling wave moving from right to left for electrodes with $W=0.2$ and $G=1.8$. (c) A vector field showing the fluid flow field above traveling wave electrodes for an applied traveling wave moving from right to left for electrodes with $W=1.8$ and $G=0.2$. 
5.1 Introduction

Recent studies have shown how the application of ac signals to micro-electrodes can cause ac electro-osmotic flow over interdigitated electrode structures [RAMOS99A, RAMOS99B, GREEN2000, GREEN2002, NADAL2002, BROWN2001, RAMOS2003, STUDER2002]. Subsequently,

\footnote{Parts of this chapter have been accepted for publication: B. P. Cahill, L. J. Heyderman, J. Gobrecht, and A. Stemmer, Electro-osmotic pumping on application of phase-shifted signals to interdigitated electrodes, Sensors and Actuators B: Chemical in press.}
micropumps were developed based on this phenomenon [Mpholo2003, Studer2004, Debesset2004]. Circulatory flow takes place over interdigitated structures with equal electrode widths while net translational flow takes place over interdigitated structures with differing electrode widths. In chapter 2, it was shown how the application of a traveling wave of potential can also cause this type of fluid flow so that the direction of travel of the traveling wave determines the direction of fluid flow [Cahill2004A]. Nevertheless, the spiral electrode structure we used to generate the traveling wave is less practical to implement as part of a microfluidic system than an interdigitated structure.

In this chapter, the principle of asymmetry suggested by Ajdari [Ajdari2000] is extended from the microfabrication of asymmetric interdigitated electrode structures to the application of phase-shifted signals to symmetrical interdigitated electrode structures. In this way the asymmetry is provided by applying phase differences other than 180°. We show how the combination of the use of practical interdigitated electrode structures with the application of phase-shifted signals results in fluid flow where the direction of travel is determined by the phase shift between the signals applied to the electrodes of an interdigitated structure. This development is made possible by adding a ground layer to the system which defines the phase difference between the ac signals applied to the electrodes.

### 5.2 Working Principles of Device

Fig. 5.1 (a) shows the form of the interdigitated electrodes structure. Fig. 5.1 (b) is a side view showing the substrate which functions as a ground layer and the electrodes are sandwiched between two insulating layers. The signals applied to the electrodes 1 and 2 are given by $V_1 = V_0 \cos(\omega t + \theta_1)$ and $V_2 = V_0 \cos(\omega t + \theta_2)$ respectively, where $V_0$ is the signal amplitude, $t$ is time, $\omega$ is the radial frequency, and the phase difference between the signals is given by $\Delta \theta = \theta_2 - \theta_1$. 

---

AC Electro-osmotic Pumping for Microfluidic Systems
AC Electro-osmotic Pumping for Microfluidic Systems
Fig. 5.2: Schematic drawings showing the principle behind how electro-osmotic flow can be caused by these electrode structures. (a) If the frequency of the signals applied to the electrodes, $\omega$, is much lower than the characteristic frequency, $\omega_c$, most of the electric field is dropped across the double layer and does not penetrate into the bulk fluid. Thus the tangential electric field is quite low and fluid flow will be insignificant. If the applied frequency is of the order of the relaxation frequency, then the fluid flow can take place depending on the amplitude of the electric double layer charge density, the amplitude of the tangential electric field and the phase difference between these two quantities. In (b) and (c) the instantaneous slip velocity is shown for a situation where the potential on each electrode has just changed its polarity and $\Delta \theta = +90^\circ$. (d) The dotted lines show the relation of the applied signals in (b) and (c). Illustration not to scale.
5.2 Working Principles of Device

Fig. 5.2 shows how phase-dependent ac electro-osmotic flow takes place over interdigitated electrode structures. The mechanism is quite similar to traveling-wave driven electro-osmosis [CAHILL2004A], the phase difference of the signals applied to adjacent electrodes plays a significant role in driving flow. The phase difference between electrodes for previously reported ac-electro-osmosis over interdigitated electrodes has been 180°. The presence of the ground layer defines the phase difference between the signals applied to the electrodes in the experiments presented in this chapter. In the small gap between the electrodes and above the electrodes, this leads to a situation that is akin to that presented in chapter 2.2 for the traveling wave electrodes. In the large gap between the electrodes, the presence of the ground layer damps the amplitude of the applied potential. Fig. 5.2 shows an approximate representation of the principle, the geometry of the structure will lead to strong electric field strengths at the electrode edges which may have a strong influence on the fluid flow.

In Fig. 5.2 (a) the frequency of the applied signal is so low that the electric double layer and electrode insulation act as capacitors in series and attenuate the applied signal so much that the applied potential does not penetrate into the bulk fluid. Also the phase difference between the electric double layer charge and the tangential electric field is such that the time average of any electro-osmotic flow that takes place is zero.

In Fig. 5.2 (b) and (c), the applied frequency approaches the relaxation frequency of the system so that the electric field penetrates into the bulk fluid and the phase difference between the electric double layer charge and the tangential electric field becomes more conducive to non-zero time-averaged electro-osmotic flow. In Fig. 5.2 (b), when the polarity of the signal applied to electrode 2 changes, the change of polarity of the ions above the electrode lags the signal. As the polarity of the ions attempts to catch up with the signal, the potential difference between the signals applied to the electrodes is close to its maximum, meaning that the tangential electric field is strong. In Fig. 5.2 (b), when the polarity of the signal applied to electrode 1 changes, the change of
polarity of the ions above the electrode also lags the signal. But as the polarity of the ions attempts to catch up with the signal, the potential difference between the signals applied to the electrodes becomes smaller, meaning that the tangential electric field becomes weaker. In this way, the asymmetry of phase of the signal applied to the electrodes means that the time average of the resulting fluid flow is biased in a particular direction.

The frequency at which this relaxation occurs depends on two mechanisms [CAHILL2004A]. First there is a resistance-capacitance (RC) relaxation due to the resistance of the fluid medium between the electrodes and the series capacitance of the electric double layer and the insulation layer. This relaxation results in an increase in the amplitude of $E_t$ at high frequencies and also a change in its phase angle. Second, the electric double layer has a characteristic relaxation time given by $\tau = \varepsilon / \sigma$. As the frequency approaches this relaxation frequency the surface charge density of the electric double layer drops and its formation begins to lag the applied signal. In a previous paper [CAHILL2004A] we explained that electric double layer relaxation need only be taken into account if the RC relaxation frequency is greater than or of the same order as the electric double layer relaxation frequency.

5.3 Materials and Methods

5.3.1 Microfabrication of Interdigitated Electrode Structures

The interdigitated electrode structures are microfabricated using the same procedure detailed in section 2.3.1 for the traveling wave electrode structures. It is important to note that the substrate is p-doped (with boron) silicon substrate coated with a 120-nm layer of silicon dioxide. The interdigitated electrode structures consist of three electrodes, see Fig. 5.1. One of these electrodes meanders from one side of the structure to the other. The other two have many single line electrodes.
connected to a main electrode. The electrode lines were 0.75 μm wide, the small gaps between the electrodes are 0.75 μm, and the large gaps are 7.75 μm wide. Fig. 5.3 is an image showing a detail of the interdigitated electrode structure.

![Interdigitated Electrode Structure](image)

Fig. 5.3: Image recorded by reflection microscopy showing a detail of the interdigitated electrode structure.

### 5.3.2 Deposition of an insulating layer

As in the experiments with the spiral electrode structures in chapter 2, the use of aluminium electrodes necessitated the use of a protective insulation layer. On analysis of the experiments it became clear that a thinner layer of a material with a higher dielectric constant would result in less potential being dropped across the insulation layer and that the electro-osmotic streaming would then take place at lower frequencies. Tantalum oxide was chosen as an insulating for the following reasons: (i) it has a relative dielectric constant of around 23, (ii) it has very high corrosion resistance against both basic and acidic aqueous electrolytes in the range pH 2-11, (iii) it has a very high dielectric strength (1 MV/cm) and (iv) it has very low pinhole density [CHRISTENSEN99]. This coating operation was performed at the IBM Zurich Research Laboratory.
5.3.3 Electrical Connections

Bonding wires were used to connect each of the electrodes to a printed circuit board. The printed circuit board (PCB) was connected by means of coaxial cables to the signal generators.

5.3.4 Details of Experimental Setup

KCl solutions in the concentration range between $10^{-4}$ M and $10^{-3}$ M were prepared and the conductivity of each was measured using a Model 115 Conductivity Meter (Orion Research Inc., Boston, MA, USA) was used for experiments. 200-nm-diameter Fluoresbrite carboxylate latex beads (Polysciences, Warrington, PA, USA) with yellow green fluorescence were suspended in the aqueous KCl solutions at concentrations of around 0.00013% v/v.

Fig. 5.4 shows the connections between the various instruments
used to perform the experiments. Two synthesized function generators (Stanford Research Systems, Sunnyvale, CA, USA) were used to generate the signals applied to the microelectrodes. By connecting the internal clock output of one to supply the external clock input of the other, it could be assured that the signals were synchronized to the same frequency. A LabView program was written to control these two function generators, a digital oscilloscope (LeCroy Waverunner, Chestnut Ridge, NY, USA), and a digital camera (Orca ER, Hamamatsu, Japan). These instruments were connected to a General Purpose Interface Bus (GPIB) interface card installed in a personal computer. The program first sets the amplitude, waveform, and frequency of signals output by the function generators. The synchronization outputs of the function generators are connected to the digital oscilloscope and the program uses the measured phase difference as input to achieve the desired phase difference. Then the digital camera records a movie sequence. The program was extended to record a set of movie sequences while performing sweeps of various parameters - frequency, amplitude, and phase.

A microscope cover slip was placed over the interdigitated electrode structure using double-sided-adhesive tape of 50-μm thickness as a spacer. After introducing the latex bead suspension into this cavity, bead movement was observed and images acquired by fluorescent light microscopy using a Nikon Eclipse 800 microscope and a digital camera. Digital movies of the latex bead movement were made after focusing a 40× objective with 0.75 numerical aperture onto the electrode surface, thus only beads within the depth of field, less than 1 μm, could be observed. Measurements of the velocity of several beads were made for each frequency and excitation potential, and the average velocity and standard deviation were calculated. The velocity was estimated by measuring the distance traveled by a bead as tracked from the digital movie and dividing by the time separating these digital movie frames.
5.4 Experiments on Interdigitated Electrodes

Fig. 5.5: Superposition of 20 thresholded images showing the movement of fluorescent beads over the electrode structure.

The observed flow depends on the signals applied to the electrodes, specifically the following parameters: phase difference, amplitude, and frequency. In addition, the flow depends quite strongly on the conductivity of the electrolytic solution. Fig. 5.5 shows a series of 20 images that were thresholded and superimposed and illustrates the movement of 500-nm diameter fluorescent latex beads. Electro-osmotic flow is generated over the electrodes and the large gap between the electrodes acts as a barrier to fluid flow. Mass continuity leads to the fluid flow taking place across the whole of the electrode structure. Albeit with a relatively high standard deviation, which can be partly attributed to Brownian motion of the 200-nm-diameter latex beads [CASTELLANOS2003]. Furthermore, as was shown in chapter 4, the slip velocity is not the same at all positions across the surface resulting in some recirculation close to the surface.

As can be seen from Fig. 5.6, at low and high frequencies the flow velocity tends to zero, while at intermediate frequencies it reaches a maximum. As the applied potential increases, the velocity increases.
Fig. 5.6: Experimentally measured values of the velocity of the fluorescent latex beads plotted against frequency at different applied potentials with amplitudes of 0.9, 1.0 and 1.1 V respectively and a phase difference of +90°. Figures (a), (b) and (c) present results obtained with the respective medium conductivities: 2.83, 5.64, and 10.65 mS/m. The fitted curves are to aid the eye.
Fig. 5.7: (a) Experimentally measured values of the velocity of the fluorescent latex beads plotted against frequency at various medium conductivities. (b) Experimentally measured values of the velocity of the fluorescent latex beads plotted against phase difference for an applied potential of 1.1 V amplitude.

Fig. 5.7 (a) shows how the electro-osmotic velocity depends on the frequency of the AC signal and on the medium conductivity. That the peak velocity decreases and the frequency of peak velocity increase with increasing conductivity is consistent with ac electro-osmotic flow as reported in chapter 2.

Fig. 5.7 (b) is a typical graph showing how the measured velocity varies with varying phase difference. The electro-osmotic velocity depends on phase difference, as the phase difference changes from negative
to positive the velocity changes from positive to negative. Thus, the
direction of flow can be reversed by changing the polarity of the phase
difference. The velocity is a maximum at phase differences of ±90°.

Fig. 5.8: The electro-osmotic velocity decreases with distance from the elec-
trodes. The channel height was 50 μm. The fitted curve is to aid the eye.

In common with results presented for traveling-wave electrode
structures in chapter 2, flow takes place in the direction of decreasing
phase angle and the use of an insulating layer results in the frequency
at which fluid flow occurs being pushed toward the electric double layer
relaxation frequency.

Fig. 5.8 shows the reduction of the electro-osmotic flow from the
slip velocity at the solid-liquid interface above the electrodes to zero
velocity at the top of the channel. The electro-osmotic flow could cause
plug flow if electro-osmotic flow was excited at both the upper and
lower interfaces.

5.5 Discussion

There are some significant differences between the experimental results
presented in this chapter with the experimental results with traveling
wave electrode structures presented in chapter 2 and modeled in chapter
3. This can be seen in the form of the presented curves and the relation of the frequency of peak velocity to the double layer relaxation frequency.

In Fig. 5.6, it can be seen that, at low frequencies, the effect of changing the applied potential is negligible and only at higher frequencies does the difference in the applied potential become significant. In Fig. 2.3, at frequencies below the frequency of peak velocity the difference in velocity is more clearly distinguishable.

Table 5.1 lists the frequencies at which the peak velocity is observed for over the interdigitated electrode structures in Fig. 5.6, the frequency that would be predicted for traveling wave structures from Eq. 3.50, and the double layer relaxation frequency. The electrolyte of lowest conductivity has a frequency of peak velocity quite close to the double layer relaxation frequency. As the electrolyte conductivity increases, the experimentally observed frequency of peak velocity becomes proportionally closer to frequency predicted by theory and less close to the double layer relaxation frequency.

Apart from the simple fact that the geometry of these interdigitated electrode structures is significantly different than the traveling wave geometry modeled in chapter 3, it is likely that the limits of the linearity of the electric double layer are exceeded so that the analysis used in chapter 3 is no longer valid. In section 3.4.6, we explained how three conditions affect the linearity of the electric double layer.

<table>
<thead>
<tr>
<th>Electrolyte Conductivity (mS/m)</th>
<th>2.83</th>
<th>5.64</th>
<th>10.65</th>
</tr>
</thead>
<tbody>
<tr>
<td>Frequency of peak velocity - theory (kHz)</td>
<td>152.7</td>
<td>304.2</td>
<td>574.6</td>
</tr>
<tr>
<td>Double layer relaxation frequency (kHz)</td>
<td>636</td>
<td>1267</td>
<td>2394</td>
</tr>
<tr>
<td>Frequency of peak velocity - experiment (kHz)</td>
<td>557</td>
<td>779</td>
<td>965</td>
</tr>
</tbody>
</table>

Table 5.1: Comparison of the difference between the frequency of peak velocity predicted by theory to the double layer relaxation frequency and to the experimentally observed frequency. The theoretical value is from Eq. 3.50 and is for a traveling wave structure with a similar insulating layer to that applied to the interdigitated electrode structure used in this chapter.
Firstly, the electrokinetic potential of the tantalum pentoxide layer used in these experiments is relatively high in contact with electrolytes of relatively low ionic concentrations. At low electrolyte concentrations, the electrokinetic potential is generally higher, see Fig. 1.2. The literature indicates that the electrokinetic potential of tantalum pentoxide is greater than $-70 \text{ mV}$ for a salt concentration of 1 mM [BOUSSE91]. Such a concentration is similar to the electrolyte with conductivity of 10.65 mS/m. The electrokinetic potential of tantalum pentoxide is greater than that of the fluorocarbon layer used in the experiments in chapter 2. The difference between the theoretically predicted value and the experimentally observed value narrows as the conductivity increases. It is likely that at lower electrokinetic potentials the validity of the theory presented in chapter 3 increases.

Secondly, in the experiments presented in this chapter, we apply potentials that are twice the amplitude of those presented in chapter 2.

Thirdly, it is likely that surface conductivity is significant for the conditions that prevail for these experiments. The combination of the high electrokinetic potential of the tantalum pentoxide surface and the high applied potential mean that the potential drop across the double layer is higher than in the experiments with the spiral electrodes. In section 3.4.6, the inverse of the propagation constant of the traveling wave was used as the characteristic length for calculating the Dukhin number, see Eq. 3.53. The characteristic length of this electrode structure is complicated by the short distance between the electrode and the ground layer, which leads to very high field strengths close to the edges of the electrodes. Such high field strengths could lead to highly non-linear effects on the formation of the electric double layer [BAZANT2004]. The Dukhin number is directly proportional to the Debye length, which in turn increases with decreasing electrolyte conductivity. The combination of higher potential drop across the electric double layer, shorter characteristic length of the electrode structure, and relatively long Debye length result in an increased Dukhin number and subsequently an increase in surface conductivity.
In dielectrophoresis, surface conductivity acts to shift the dielectrophoretic relaxation to higher frequencies [HUGHES99]. The mechanism for this shift of the dielectrophoretic relaxation time is the extension of the formation of the electric double layer around a colloidal bead to frequencies above the double layer relaxation frequency if two conditions are fulfilled. Firstly that the electrokinetic potential is high and secondly that the radius of the bead is small. For the case of ac electro-osmosis, it is likely that surface conductivity also acts to cause the deviation of the frequency of peak velocity from that predicted by theory.

The dependence of the frequency of peak velocity on electrolyte conductivity is not as predicted by theory. It is reasonable to assume that this deviation can be explained by higher surface conductivity at lower electrolyte concentration. The variation in surface conductivity is because both the Debye length and the electrokinetic potential tend to increase with decreasing conductivity.

5.6 Conclusion

In these experiments, it was shown how translational flow can be achieved above an interdigitated electrode structure if a ground layer is added to the system so that the phase difference between the applied signals is defined. In this way, translational fluid flow similar to that caused by traveling waves in chapter 2 can occur and the direction of flow can be controlled externally by varying the phase difference of the signals applied to the electrodes. The microfabrication of electrode structures with feature sizes of below 1 \( \mu m \) makes it possible to pump aqueous electrolytes at velocities of up to 100 \( \mu m/s \) on application of potentials of below 1 \( V_{rms} \). Furthermore the use of a ground layer results in even higher field strengths being generated at the electrode edges. The low-amplitude potentials required can be supplied by cheap batteries and are a major advantage for the implementation of ac electro-osmosis in lab-on-a-chip systems.
Chapter 6

Conclusions

6.1 Summary

This thesis concentrates on electro-osmotic flow of electrolytes on application of alternating potentials to electrode structures. Specifically this thesis examines the application of phase shifted signals to electrodes.

In a first implementation, traveling waves of potential are used to excite electro-osmotic flow. A spiral electrode structure was microfabricated for this purpose. Experiment shows that electro-osmotic streaming of electrolytes with conductivity in the range of 2 - 8 mS/m can be driven by applying traveling-wave signals.

In comparison with previously reported forms of ac electro-osmotic flow, translational flow was achieved using traveling waves where changing the direction of travel of the traveling wave reverses the direc-
tion of streaming, thus allowing flexible external control. Nevertheless, the use of asymmetry suggested by Ajdari [Ajdari2000] does result in electrode structures that are more practical to fabricate and use. In a second implementation, an interdigitated structure is employed to drive electro-osmotic flow above interdigitated electrodes. The addition of a ground layer, allows the use of phase shifted signals to excite electro-osmotic flow where the direction of flow is dictated by the phase shift between the signals applied to the electrodes. In this way, the phase difference between the electrical signals applied to the electrodes is asymmetric rather than the geometry of the electrodes used to excite the flow.

Two theoretical models were derived which describe such electro-osmotic flow on application of a traveling wave potential as a function of the amplitude of the applied electrical potential, the signal frequency and the material properties of the system. The direction of streaming, the relationship of applied potential to velocity, and the frequency of maximum velocity with varying medium conductivity frequency agree well with that predicted by Eq. (3.50).

Simulation of the flow profile shows that the use of a traveling wave electrode structure leads to an avoidance of the recirculation that is observed for ac electro-osmosis driven by interdigitated electrodes with asymmetric electrode width. Although the flow profile exhibits some waviness close to the electrodes, at distances from the electrodes greater than one electrode width, linear flow in the direction of motion of the traveling wave is predicted. The waviness of the flow profile close to the electrodes may contribute to high standard deviation of the experimentally observed velocity.

In common with other forms of electro-osmotic flow, this method has a pronounced advantage over pressure-driven flows because it continues to pump effectively as the dimension of the channel is reduced. For pressure-driven flows, the pressure gradient must increase as the square of the inverse of channel size to maintain a given fluid speed. In addition, pressure-driven flows often require external equipment, which is a ma-
6.2 Outlook

6.2.1 Generation of True Plug Flow

The use of the phenomena presented in this thesis requires the microfabrication of a microfluidic system where pumping is generated on both upper and lower channel surfaces [MPHOLO2003, STUDER2004, DEBESSET2004]. The prospect of ac electro-osmotic flow generating plug flow has driven the interest in this phenomenon [AJDARI2000]. Nevertheless, there are some challenges to fully achieving this goal.

Firstly, the effect of the no-slip condition at the channel side walls will result in a Poiseuille flow profile in the lateral direction. It may be possible to overcome this problem by constructing a microfluidic system without sidewalls. Zhao et al. [ZHAO2001] implemented a microflu-
idic channel system by patterning a self-assembled monolayer (SAM) to define hydrophobic and hydrophilic areas. The surface wetting properties of the surface thus define the "microfluidic channel". Recently the use of microfabrication not only to define the wetting properties of the surface but also to induce superhydrophobicity has been presented [LAFUMA2003]. A microfluidic system with the channel walls defined by the surface wetting properties could enable the construction of an ac electro-osmotic pump capable of generating true plug flow.

Secondly, the vertical disturbance of traveling wave ac electro-osmotic flow described in chapter 4 is of the order of the width of the electrodes. It is also true that the experimentally observed velocity of ac electro-osmosis above interdigitated electrodes on application of phase-shifted signals described in chapter 5 exhibits high standard deviations close to the electrode surface.

Thirdly, it is not possible to increase the flow velocity indefinitely by simply increasing the voltage. The relation to the square of applied potential presented in Fig. 2.4 is dependent on the application of low potential. Outside of the limits discussed in section 3.4.6, ac electro-osmosis becomes highly non-linear. At Nanotech 2003 in Montreux, Nicolas Green reported the reversal of flow direction at higher applied potentials and this phenomenon has been confirmed by Studer et al. [STUDER2004]. Neither offered an explanation for this reversal of direction. On applying high-strength electric fields to aqueous electrolytes ohmic heating of the fluid may lead to other effects predominating over electro-osmosis.

6.2.2 Application of AC Electro-osmosis in Micro Fuel Cells

Much interest is being shown in the development of micro fuel cells to replace the lithium ion batteries that are used in portable electronic devices and telecommunications devices. Xie et al. [XIE2004] of Motorola identify a mixture of distilled water and methanol as the fuel most likely
to find commercial application. They used an off-the-shelf diaphragm air pump to drive pumping in their system but expressed reservations about the suitability of this pump with regard to its bulk, noisiness and short lifetime. Yen et al. [Yen2003] and Lu et al. [Lu2004] each used an external peristaltic pump to deliver an aqueous methanol mixture to a microfabricated fuel cell. An ac electro-osmotic pump is well suited to pumping such a water-methanol mixture as the conductivity of which is lower than the electrolytes used in the experiments presented in this dissertation. More importantly it is imperative that the power consumption of the pumping method used in the microfuel cell is low so that the overall efficiency of the fuel cell is high. It is likely that the low potential required to drive ac electro-osmosis can be supplied by such a fuel cell and that an ac electro-osmotic pump fulfills the efficiency requirements of such a fuel cell.
AC Electro-osmotic Pumping for Microfluidic Systems
Bibliography


AC Electro-osmotic Pumping for Microfluidic Systems
<table>
<thead>
<tr>
<th>Reference</th>
<th>Details</th>
</tr>
</thead>
</table>

AC Electro-osmotic Pumping for Microfluidic Systems


AC Electro-osmotic Pumping for Microfluidic Systems


AC Electro-osmotic Pumping for Microfluidic Systems
AC Electro-osmotic Pumping for Microfluidic Systems

[BIBLIOGRAPHY]


AC Electro-osmotic Pumping for Microfluidic Systems


**AC Electro-osmotic Pumping for Microfluidic Systems**
AC Electro-osmotic Pumping for Microfluidic Systems
Appendix A

Electrical Circuits

The following figures show the components of the four-phase square-wave generator described in section 2.3.4.
Fig. A.1: An externally connected input signal is used as the input to a shift-register integrated circuit that delivers four output square waves that are separated from each other by 90°. The output signal is at a frequency four times smaller than the input signal. The input signal is converted from a sine wave to a rectified square wave of the same frequency in the stage before the shift register.

Fig. A.2: Schematic of the power supply for the circuit.
Fig. A.3: Schematic of the amplitude control input. The user turns a potentiometer which controls the voltage $V_g$. $V_g$ is the input to the amplifier in Fig. A.4 below.

Fig. A.4: The output signals from the shift register in Fig. A.1 are each amplified by an amplifier of the type shown in this figure and the end signal is output to a BNC connector.

AC Electro-osmotic Pumping for Microfluidic Systems
Curriculum Vitae

Personal Data

Name: Brian Patrick Cahill  
Date of Birth: 10th of July 1974  
Place of Origin: Dublin, Ireland  
Nationality: Irish

Education

1986-1991 Synge Street CBS, Dublin, Ireland  
1991-1995 Dept. of Mechanical Engineering  
        University College Dublin (UCD)  
        Degree: BE in Mechanical Engineering  
1996-1998 Dept of Mechanical and Manufacturing Engineering  
        Dublin City University (DCU)  
        Master’s thesis: Fibre-optic sensor for measuring  
        surface roughness and displacement  
        Degree: MEng (Master of Engineering)  
2000-2004 Nanotechnology Group  
        Eidgenössische Technische Hochschule Zürich (ETH)  
        (Swiss Federal Institute of Technology)  
        Thesis Advisors: Prof. Dr. A. Stemmer, ETH Zurich,  
        Prof. Dr. O. J. F. Martin, EPF Lausanne, and  
        Dr. H. F. Knapp, CSEM, Alpnach.

Professional Experience

1998-2000 Optical Communication Measurements Division,  
        Agilent Technologies, Böblingen, Germany  
        Learning Products Engineer