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AC Asymmetric Electrode Micropumps

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Abstract

The ability to move minute amounts of fluid around in a liquid circuit has become an increasingly important feature in current lab-on-a-chip systems. Several methods have previously been suggested, yet they lack the simplicity offered by the new and promising technique of Induced Charge electroosmotic pumping.

In the present project, AC asymmetric electrode micropumps based on the principles of Induced Charge electroosmosis were designed and fabricated using standard cleanroom processing techniques. The micropumps were subsequently electrically characterized and a corresponding equivalent diagram model has been evaluated. In addition, a one dimensional model of a two electrode system has been analytically examined for an asymmetric electrolyte.

Experimental flow velocities in the order of $140 \,\mu\text{m/s}$ at $1.5 \,V_{\rm rms}$ corresponding to velocities of $\sim 0.5 \,\text{mm/s}$ above the electrodes have been obtained. These velocities are compared with current theory. Furthermore, the parameter space of the micropump has been investigated and especially the effect of alterations in the applied voltage, the electrode translation period and the electrolytic concentration has been thoroughly studied.

ABSTRACT

Resumé

Evnen til at kunne flytte små væskemængder rundt i et lukket kredsløb af mikrokanaler er blevet en stadig vigtigere egenskab indenfor udnyttelsen af lab-on-a-chip systemer. Adskillige metoder er blevet foreslået, dog mangler de den simplicitet som karakteriserer den nye og lovende elektroosmotiske pumpeteknik vha. vekselspænding.

AC asymmetrisk elektrode mikropumper, som er baseret på principperne omkring ladningsinduceret elektroosmose, er i det foreliggende projekt blevet designet og fremstillet. En elektrisk karakteristik blev siden udarbejdet for disse mikropumper, og et tilhørende ækvivalensdiagram er blevet evalueret. Ydermere er en en-dimensional model af et toelektrode-system indeholdende en asymmetrisk elektrolyt blevet underkastet en analytisk behandling.

Eksperimentelle strømningshastigheder i størrelsesordenen 140 μ m/s ved 1.5 V_{rms}, svarende til hastigheder på ca. ~ 0.5 mm/s over elektroderne, er blevet påvist. Disse hastigheder sammenlignes her med gældende teori på området. Herudover er væsentlige variable parametre for den omtalte mikropumpe blevet undersøgt med særligt fokus på de virkninger der kan observeres når der foretages ændringer i den påtrykte elektrode-spænding, elektrodernes translationsperiode samt koncentrationen af elektrolytter.

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Preface

This thesis, titled "AC Asymmetric Electrode Micropumps", has been submitted in order to obtain the Master of Science degree at the Technical University of Denmark (DTU). Project work was carried out within the Microfluidic Theory and Simulation (MIFTS) group at the Department of Micro- and Nanotechnology (MIC), DTU during the period from October 2004 to October 2005 under supervision by Henrik Bruus and Mikkel Fought Hansen.

First of all I would like to thank my supervisors Henrik and Mikkel for their support and sound advice throughout the project. Furthermore, sincere appreciation also goes to Ph.D. students Anders Brask and Laurits Højgaard Olesen for their assistance with respectively the experimental and theoretical aspects of the project and their almost endless patience. Moreover, I have also appreciated the good ideas and solutions offered by the rest of the MIFTS group, especially at group meetings, whenever problems had arised.

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Finally, a big thanks to all those not mentioned above, but who have offered their assistance or helped me in one way or another during this project.

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List of symbols

Symbol	Description	Unit
x	Position vector	m
$oldsymbol{v}$	Velocity vector	${\rm m~s^{-1}}$
v	Velocity	${\rm m~s^{-1}}$
σ	Cauchy stress tensor	${ m N~m^{-2}}$
f	Body force density	${ m N~m^{-3}}$
g	Gravitational acceleration	$ m N~kg^{-1}$
\boldsymbol{n}	Surface outward normal vector	
p	Pressure	${ m N~m^{-2}}$
μ	Dynamic viscosity	$\rm kg \ m^{-1} \ s^{-1}$
T	Temperature	Κ
σ	Electrical conductivity	$J \ K^{-1} \ m^{-1}$
Q	Volume flow rate	${ m m}^{3}~{ m s}^{-1}$
j	Particle current density	${\rm m}^{-2}~{\rm s}^{-1}$
J	Mass current density	$\rm kg \ m^{-2} \ s^{-1}$
i	Charge current density	${ m A~m^{-2}}$
ho	Mass density	${ m kg}~{ m m}^{-3}$
ho	Charge density	${ m C}~{ m m}^{-3}$
c	Ionic density	m^{-3}
D	Diffusion coefficient	$\mathrm{m}^2~\mathrm{s}^{-1}$
ϕ	Electric potential	V
μ	Chemical potential	$\rm J~mol^{-1}$
λ_D	Debye length	m
ϵ	Permittivity	${\rm F}~{\rm m}^{-1}$
Z	Ionic valence	

LIST OF SYMBOLS

Chapter 1

Introduction

Lab-on-a-chip systems have been developed and optimized for various applications within a broad range of advancing scientific fields. Sample analysis in chemistry, biochemistry and the pharmaceutical industry may be optimized regarding sample consumption, automation and portability using new sample handling and measurement techniques. The components of the analysis systems are significantly down-scaled compared to standard analytical devices, which facilitatates a large-scale production and thus leads to inexpensive systems. One example on a direct application of a complete lab-on-a-chip system could be a portable analysis system for rapid control of water quality.

1.1 Micropumps in lab-on-a-chip systems

The complexity of microfluidic devices are continously increasing, and full control of liquid motion is now required. Integrated micropumps and valves are viewed as necessary for this purpose. Within the last decade, two main categories of pumping systems have been proposed for lab-on-a-chip applications. One category employs mechanical actuators, such as deflectable membranes or moving walls, to create valves and pumps. Unfortunately, micropumps utilizing these principles will be difficult to down-scale more than the presently achieved dimensions. The second category of pumps utilizes alternating electric fields generated by a low-voltage signal applied to micro-fabricated electrodes, which induces electrokinetic pumping. In contrast, the classical DC electroosmotic pumping systems require high voltages and thus introduce difficulties regarding Joule heating and bobble formations, occuring as a result of electrochemical reactions at the electrodes.

Recently, AC electroosmosis has been observed to induce fluid motion over a pair microelectrodes [5, 6]. Ajdari proposed a model of fluid motion above an electrode array covered by an electrolyte and biased by an AC signal. It was concluded that a net pumping effect could be obtained by introducing asymmetry in the system [1]. Brown *et al.* [7] demonstrated experimentally this Induced Charge effect shortly after. Later, several other groups reported Induced Charge (IC) pumping velocities of up to approximately 1 mm/s [8, 9]. Studer *et al.* [3] made a comprehensive investigation of voltage and frequency variations, which gives an overview of the IC electroosmosis. In addition to this, the electrolytic concentration was also varied. Expectable tendencies were reported, but several unexplainable effects were also observed.

The IC electroosmotic pumping method is easier to down-scale and integrate than the DC method, and it is fully compatible with the microfabrication technology because of the simple construction.

1.2 Objective and motivation

Simulations of the IC electroosmotic pumps performed during the last two years by Mortensen *et al.* [2] and Olesen *et al.* [4] have shown interesting nonlinear effects from investigations of the parameter space. Motivated by these investigations, experimental projects have been initiated in order to examine the effects of corresponding parameter variations. A first attempt to produce the pumps was made during the B.Sc. project of Arnoldus and Hansen [19]. A rather complicated micropump device was designed and fabricated using standard cleanroom processing, however, no pumping was observed. It was concluded that the device geometry was too complex and the fabrication process unreliable.

The scope of the present project has been to make another attempt at fabricating an IC electroosmotic micropump. Taking the work of Studer *et al.* [3] as a starting point, a simpler micropump construction had to be developed. Furthermore, the fabrication should be based on standard cleanroom processing, and process flow different from that of Arnoldus and Hansen needed to be established. The micropump should not be constructed for actual pumping purposes, but instead for basic studies of the hydrodynamic system. It has been the aim of this project to investigate the variation of relevant parameters in accordance with the performed numerical simulations.

1.3 Thesis outline

During the project, a rather large part of the available time was spend designing and manufacturing the micropump devices. The fabrication caused unforeseen problems which ended up being very time consuming. The devices were nevertheless successfully completed and time was afterwards spend building the measurement setups before the actual tests could be performed. A minor part of the entire project time was spend performing analytical calculations. The chapters of the present thesis contains following:

- Chapter 2: Basics of hydrodynamics and electrohydrodynamics.
- Chapter 3: Theory and basic models of the Induced Charge electroosmotic micropumps are presented. An analytical one dimensional calculation of a two electrode system for an asymmetric electrolyte is performed.
- Chapter 4: The final micropump design is presented. Considerations and estimates behind the design are explained.

1.3. THESIS OUTLINE

- Chapter 5: The process flow is described along with challenges and considerations encountered during fabrication.
- Chapter 6: Measurement setups for all performed experiments are presented.
- Chapter 7: Results of the electrical characterization of the micropumps are presented. The measurements are compared with an equivalent circuit model.
- Chapter 8: The obtained flow measurements are shown and compared with current theoretical results.

Chapter 2

Microfluidics

The fundamental theory of hydrodynamics is based on the continuum hypothesis, where a fluid is regarded as a single continuous phase with all macroscopic quantities smoothly distributed within a volume of interest and specified for each infinitesimal volume element, independent of the real molecular fluid structure. This assumption is valid when the characteristic length scale of a given fluidic system is much larger than the scale of molecular correlations and fluctuations, which are in the order of 10 nm. As the word suggests the typical length scale in microfluidic systems is at least a couple of micrometers which is enough to make the hypothesis applicable and a classical description possible.

The flow character is also important for the mathematical description of a fluidic system. Turbulent flow has a rather complex nature and is often chaotic while laminar streaming is easier to express and predict. The Reynolds number Re of a specific fluidic system indicates which kind of flow the system supports depending on whether inertial forces or viscous forces are dominating. $Re \equiv \rho V L/\eta$, where V and L are respectively the characteristic velocity and length of the given system, ρ is the mass density of the fluid and η the viscosity. When viscous forces dominates, laminar flow is expected corresponding to a Reynolds number much less than one. In microfluidic systems the small length scale and limited velocities clearly lead to smaller Reynolds numbers, which implies that laminar flow patterns are common in these systems¹.

In the following hydrodynamic description, two fundamental assumptions are utilized regarding the liquids considered in the present project. First the fluids are assumed to be Newtonian that is, they follow the Newtonian viscosity law stating that the shear stresses are linearly related to the rates of strain [12]. This is a good approximation for gases and simple liquids, and implies that the viscosity η is a constant. Since only liquids are considered in the project, a second assumption is to regard the fluid as being incompressible, i.e. having a constant mass density ρ . This approximation is reasonable when the considered flow velocity of the fluid is much less than the velocity of sound in the liquid and its application will later become apparent.

¹For $L = 1 \,\mu\text{m}$, $V = 1 \,\text{mm/s}$, $\rho = 10^3 \,\text{kg/m}^3$ and $\eta = 1 \,\text{mPa s}$, the Reynolds number is $Re = 10^{-3} \ll 1$.

2.1 Governing equations

The motion of fluids is governed by the conservation equations of mass and momentum in a fluidic system. If also heat transfer due to electrical heat generation or internal viscous dissipation within a fluidic system should be considered, the equation of energy conservation has to be taken into account along with the aforementioned equations. In the present project the internal heat flows will not be analyzed, and in the following only the equations ensuring conservation of mass and momentum are presented in an Eulerian reference frame, i.e., relative to fixed points in space. The velocity field of the fluid \boldsymbol{v} is introduced, and the mass current density is expressed as $\boldsymbol{J}(\boldsymbol{r},t) = \rho(\boldsymbol{r},t) \, \boldsymbol{v}(\boldsymbol{r},t)$.

2.1.1 Continuity equation

Within a specified volume, the rate of mass change may be expressed in two ways. Either by the time derivative of the total mass within the given volume, expressed through the mass density ρ or by the total mass current streaming out of the volume, specified by the mass current density J. Equalizing these rates of change results in the continuity equation describing conservation of mass for a newtonian fluid:

$$\partial_t \rho + \nabla \cdot \boldsymbol{J} = 0 \quad \text{or} \quad \partial_t \rho + \nabla \cdot (\rho \, \boldsymbol{v}) = 0.$$
 (2.1)

If now ρ is regarded as constant and the fluid is said to be incompressible, the continuity equation takes the more simple form

$$\boldsymbol{\nabla} \cdot \boldsymbol{v} = 0. \tag{2.2}$$

2.1.2 Navier–Stokes equation

Macroscopically, the conservation of momentum for a Newtonian fluid system is expressed through Newton's second law applied to a fluid unit volume, moving through the system,

$$\rho D_t \boldsymbol{v} = \boldsymbol{f}_{\text{body}} + \boldsymbol{f}_{\text{surf}}.$$
(2.3)

The substantial derivative $D_t \equiv \partial_t + (\boldsymbol{v} \cdot \boldsymbol{\nabla})$ is utilized since the rate of change of the velocity field is expressed for a unit volume following the fluid flow. The right hand side of the equation shows that two kinds of force densities have an impact on the fluid. The body force densities, which are proportional to the density of the fluid, and the surface force densities generated by the external stresses on a fluid unit volume, expressed through the stress tensor. The stress tensor can be written as a sum of the pressure on a fluid unit volume and the viscous stress tensor, arising from the frictional forces within the fluid. Then, for incompressible fluids with constant viscosity η the surface forces are normally expressed in two terms, a pressure gradient force $-\boldsymbol{\nabla}p$ and a viscous force $\eta \nabla^2 \boldsymbol{v}$. The equation of momentum conservation, also termed the Navier–Stokes equation, then takes the following form [16];

$$\rho D_t \boldsymbol{v} = \rho \left[\partial_t \boldsymbol{v} + (\boldsymbol{v} \cdot \boldsymbol{\nabla}) \boldsymbol{v} \right] = -\boldsymbol{\nabla} p + \eta \nabla^2 \boldsymbol{v} + \boldsymbol{f}_{\text{body}}.$$
(2.4)

2.2. DIFFUSION

Examples of the unspecified body forces are the gravitational force, proportional to the acceleration of gravity, $f_{\text{grav}} = \rho g$, and the electrical force, specified by an electrical field \boldsymbol{E} applied to a fluid with a given charge density ρ_{el} as $f_{\text{el}} = \rho_{\text{el}} \boldsymbol{E}$.

Eqs. (2.2) and (2.4) are adequate to describe the fluid motions of an incompressible and isothermal liquid with constant viscosity, when the boundary conditions of the relevant system are specified. However, the nonlinear term $(\boldsymbol{v} \cdot \boldsymbol{\nabla}) \boldsymbol{v}$ in the Navier–Stokes equation, makes the equation non-trivial to solve. In microfluidic systems though, it will often be possible to neglect this term and get approximate solutions with a minor deviation from the actual flow pattern. The variables of a microsystem may be scaled according to the characteristic parameters of the system, resulting in a dimensionless form of the Navier– Stokes equation. If the dimensionless variables are denoted with a tilde, Eq. (2.4) takes the form [16]

$$Re\left[\tilde{\partial}_t \tilde{\boldsymbol{v}} + (\tilde{\boldsymbol{v}} \cdot \tilde{\boldsymbol{\nabla}}) \tilde{\boldsymbol{v}}\right] = -\tilde{\boldsymbol{\nabla}} \tilde{\boldsymbol{p}} + \tilde{\nabla}^2 \tilde{\boldsymbol{v}}.$$
(2.5)

The Reynolds number is hereby determined as $Re \equiv \rho V L/\eta$, where L is the characteristic length scale of the system and V is the characteristic velocity. Thus, microscale systems have low Reynolds numbers, and Eq. (2.5) implies that viscous forces dominate relative to inertial forces in these systems.

2.2 Diffusion

Diffusion arises from the random thermal motion of molecules in a heterogeneous solution and is the resulting overall flux of molecules along negative concentration gradients of the individual species. For dilute solutions the components of the fluid can be considered as independent, and more specifically each species can be treated separately. In this case it is stated by Fick's first law of diffusion that the diffusive flux density or diffusion current density J_i^{diff} of a given species is proportional to the concentration gradient, i.e., to spatial variations in the species mass density ρ_i [16],

$$\boldsymbol{J}_{i}^{\text{diff}} = -D_{i}\rho\,\boldsymbol{\nabla}n_{i}.\tag{2.6}$$

The concentration is defined as the relative mass density, $n_i = \rho_i / \rho$, and the proportionality constant D_i is the diffusivity or diffusion coefficient of the species *i*. Some common values are listed in Table 2.1.

The total mass current density J_i of a single component in a heterogeneous solution now consists of two terms, the current density due to convection J^{conv} in the moving liquid with velocity field v and a diffusion current density J^{diff} , so that $J_i = J_i^{\text{conv}} + J_i^{\text{diff}}$. This must be taken into account when writing the continuity equation of an individual species

	H^+	OH-	K^+	Cl-	Na ⁺	KCl	NaCl
Diffusivity, $D_i [10^{-9} \mathrm{m^2/s}]$	9.31	5.30	1.96	2.03	1.33	1.994	1.612

Table 2.1: Diffusivity of some ions and electrolytes at infinite dilution in water at 298K [16, 12].

in a solution. Utilizing also the continuity equation, Eq. (2.1), valid for the total solution, results in the convection-diffusion equation for solutes in dilute solutions:

$$\partial_t n_i + \boldsymbol{v} \cdot \boldsymbol{\nabla} n_i = D_i \, \nabla^2 n_i. \tag{2.7}$$

A dimensional analysis of the convection-diffusion equation makes it reasonable to introduce the Péclet number Pe, which expresses whether convection or diffusion dominates in a given fluidic system. If V_0 is the characteristic velocity of the system, D is the diffusion constant of a certain solute and L_0 is the characteristic length scale of the concentration variation, the diffusion Péclet number is given by [16]

$$Pe = \frac{\text{diffusion time}}{\text{convection time}} = \frac{L_0^2/D}{L_0/V_0} = \frac{V_0 L_0}{D}.$$
(2.8)

When the velocity field of a fluid system is zero, there is no convection present and Eq. (2.7) becomes the diffusion equation,

$$\partial_t n_i = D_i \, \nabla^2 n_i. \tag{2.9}$$

Dimensional analysis of this equation gives a good indication of the relation between the characteristic timescale T_0 and length scale L_0 of the concentration variation in the system,

$$L_0^2 = D T_0. (2.10)$$

Here it is assumed that only one species is present.

To get an impression of how the system variables influence the diffusion coefficient of a given solute in a liquid, the forces on a single solute particle are considered. The diffusion force is calculated from thermodynamics as the change in Gibbs free energy when the particle is added the solution. This is expressed through the chemical potential μ_i of the solute [12],

$$\mu_i(\boldsymbol{r}) = \mu_{i,0} + k_{\rm B}T \ln\left(\frac{c_i(\boldsymbol{r})}{c_{i,0}}\right).$$
(2.11)

where $\mu_{i,0}$ is a reference chemical potential of the solution and $c_{i,0}$ the corresponding reference particle concentration, c_i is the actual particle concentration of the species and T the temperature of the suspension. Considering only translational diffusion of the suspended particle, the diffusion force given by the negative gradient of the chemical potential is balanced by the Stokes drag force, which for a spherical particle of radius Rin a liquid of viscosity η is $\mathbf{F}_{\text{drag}} = 6\pi\eta R \mathbf{v}$. Invoking Fick's law, Eq. (2.6) in the form $\mathbf{j}_i = -D_i \nabla c_i$ where $\mathbf{j}_i = c_i \mathbf{v}$ is the particle current density, results in the Stokes–Einstein relation,

$$D = \frac{k_{\rm B}T}{6\pi R\eta}.\tag{2.12}$$

Eqs. (2.10) and (2.12) may be used to give an estimate of the diffusion time of a given solute in a relevant system. In the present project, beads with a diameter of 1 μ m are loaded into an aqueous solution. The diffusivity of these beads will then be approximately $D_{\text{beads}} = 4.4 \times 10^{-13} \text{ m}^2/\text{s}$, and consequently the beads will be able to spread out on $26 \ (\mu \text{m})^2$ within 1 min if only the diffusion force is present.

2.3 Basic flow patterns

Returning to the Navier–Stokes equation, Eq. (2.4), a few analytical flow solutions exist. In some particular cases, spatial symmetries causes the nonlinear inertia term to become zero, leaving a much simpler linear equation to solve. These solutions of quite simple and highly symmetrical flow systems may be very usable since many microfabricated systems are rather easily approximated by a simpler geometry, resulting in good predictions of actual flow patterns. In this section, two of the most basic flow types are briefly presented for a geometry much alike the channel structure fabricated and used in the present project; a long and straight channel with rectangular cross section of height h very much smaller than the width w. The channel of length L is placed with the x-axis along the flow direction and the channel height is given in the direction of the z-axis. The flow generation within the fabricated microchannels may be approximated by a Couette flow, which is presented below. A pressure difference applied over the channel ends adds a Poiseuille flow to the total flow through the channel, and this is explained in the next subsection.

2.3.1 Couette flow

One of the Navier–Stokes solutions that are possible to obtain analytically, is the mechanically induced Couette flow generated by moving a solid surface relative to the liquid. Having a very wide rectangular channel makes it reasonable to look at a geometry consisting of two infinitely wide parallel plates, i.e. the effect of the channel sidewalls are neglected, since this simplification reduces the dimension of the problem. Now positioning the plates in the xy-plane perpendicular to the gravitational acceleration along the z-axis, a flow is generated by moving the top plate along the x-axis. Utilizing the no-slip boundary condition, which implies that the fluid should be at rest at the channel walls, results in a liquid velocity field consisting of only an x-component dependent on the position z in the channel, $\mathbf{v} = v_x(z) \mathbf{e}_x$. A velocity field of the this form leads to a zero nonlinear inertia term, $(\mathbf{v} \cdot \nabla)\mathbf{v}$, and in steady state the Navier–Stokes equation takes the simple form [16],

$$\mathbf{D} = \eta \nabla^2 \boldsymbol{v}.\tag{2.13}$$

No pressure or body forces are affecting the flow, as the gravitational body force is balanced by a vertical hydrostatic pressure gradient, $p_{eq}(z) = -\rho gz$, originating from the reaction forces of the bottom plate.

Solving Eq. (2.13) and applying the no-slip boundary conditions, specified by the velocity v_0 of the top plate relative to the bottom plate at rest, gives rise to the following linear velocity profile, see Fig. 2.1a,

$$v_x(z) = v_0 \frac{z}{h}.\tag{2.14}$$

The flow rate, Q, of the channel is calculated by integration of the velocity field, $v_x(z)$, with respect to the channel cross section in the yz-plane:

$$Q = \int_0^w dy \int_0^h dz \, v_x(z) = \frac{1}{2} \, v_0 \, h \, w.$$
 (2.15)



Figure 2.1: The velocity profiles between two infinitely wide parallel plates of a) a Couette flow generated by moving the top plate with velocity v_0 relative to the bottom plate and b) a Poiseuille flow driven by the pressure difference Δp over the ends of channel.

2.3.2 Poiseuille flow

The Poiseuille flow or pressure driven flow is another problem, which is possible to solve analytically from the Navier–Stokes equation if the geometries are chosen properly. Again, a horizontally placed, long, straight and stiff channel is considered, and this time a pressure difference Δp is applied over the ends of the channel. The mathematical form of the liquid velocity field is quite similar to that of the Couette flow problem. If the pressure difference is applied exclusively along the x-direction, the velocity field will be of the form $\boldsymbol{v} = v_x(y, z) \boldsymbol{e}_x$, once more leaving a zero inertia term. Only the pressure is considered as an external force and as the gravitational body-force once more is outbalanced by the hydrostatic pressure gradient, the Navier–Stokes equation, governing the flow when steady state is reached, becomes

$$\mathbf{0} = \eta \nabla^2 \boldsymbol{v} - \boldsymbol{\nabla} p. \tag{2.16}$$

This equation is solved by separation of variables, invoking respectively the boundary conditions of the pressure p_0 and $p_0 + \Delta p$ and the no-slip boundary conditions of the velocity field.

Flow between infinite parallel plates

For infinitely wide parallel plates, where the effect of the channel side walls is neglected, the velocity field directed along the x-axis only depends on the z-coordinate, $\boldsymbol{v} = v_x(z) \boldsymbol{e}_x$. Applying the no-slip boundary condition with zero velocity at z = 0 and z = h results in the following parabolic velocity profile, also shown at Fig. 2.1b,

$$v_x(z) = \frac{\Delta p}{2\eta L} (h - z)z. \tag{2.17}$$

Now integrating the velocity profile over the channel cross section leads to a basic relation between the pressure difference applied over the channel ends and the flow rate through the channel:

$$\Delta p = \frac{12\eta L}{h^3 w} Q = R_{\text{hyd}} Q. \qquad (2.18)$$

The proportionality constant is denoted the hydraulic resistance R_{hyd} .

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Flow in rectangular channel

As mentioned above, the channels used in the present project can be regarded as long, straight channels of rectangular cross-sections, motivating the following investigation of this geometry. Despite being a highly symmetrical flow problem, it is not possible to obtain an analytical expression for the velocity profile. Instead, the solution may be represented by a Fourier sum [16]

$$v_x(y,z) = \frac{4h^2 \Delta p}{\pi^3 \eta L} \sum_{n,\text{odd}}^{\infty} \frac{1}{n^3} \left[1 - \frac{\cosh(n\pi \frac{y}{h})}{\cosh(n\pi \frac{w}{2h})} \right] \sin\left(n\pi \frac{z}{h}\right).$$
(2.19)

Integration of Eq. (2.19) with respect to the channel cross section gives rise to the following relation between pressure and flow rate. A normalized contour plot of the flow rate is shown at Fig. 2.2.

$$Q = \frac{h^3 w \Delta p}{12\eta L} \left[1 - \sum_{n,\text{odd}}^{\infty} \frac{1}{n^5} \frac{192}{\pi^5} \frac{h}{w} \tanh\left(n\pi \frac{w}{2h}\right) \right].$$
 (2.20)

For $h/w \ll 1$ a simplified, but quite accurate² expression of Eq. (2.20) is found,

$$Q \approx \frac{h^3 w}{12\eta L} \left[1 - 0.630 \, \frac{h}{w} \right] \Delta p. \tag{2.21}$$

Comparison of Eq. (2.21) and Eq. (2.18) shows that the flow rate error introduced by approximating a channel of rectangular cross section with two infinitely wide parallel plates is of the order h/w.



Figure 2.2: Contour plot of the Poiseuille flow rate, Eq. (2.20), in a channel having dimensions equal to the channels fabricated in the present project. Notice that the two axis are not drawn to scale in order to emphasize the shape of the flow rate.

2.4 Electroosmotic flow

Continuing the presentation of governing equations and important relations of a microfluidic system, electrohydrodynamics is the next subject to be treated in this section. Here, it is considered how ions are distributed in a hydrodynamic system, and how they move when electric fields are applied to the system, thereby adding a body-force to the charged particles in the solution.

²For an aspect ratio of w/h = 2 the simplification introduces an error of only 0.2% [16].

Poisson equation

The currents and electric fields in such a fluidic system containing charged species are fully governed by Maxwell's equations and Ohm's law. Furthermore it is assumed that no magnetic fields are present and if also the induced fields are neglected the problem becomes entirely electrostatic. Maxwell's equations lead to the well-known Poisson equation, relating the electrostatic potential ϕ and the spatial charge distribution $\rho_{\rm el}$:

$$\nabla^2 \phi(\mathbf{r}) = -\frac{1}{\epsilon} \rho_{\rm el}(\mathbf{r}). \tag{2.22}$$

Conductivity of liquids

When ions in a fluidic system are exposed to an electric field they will move with a velocity $\boldsymbol{v}_{\rm ep}$ proportional to the size of the field \boldsymbol{E} . The proportionality constant is defined as the ionic mobility $\mu_{\rm ion}$ and depends on the type of ions as well as the surrounding liquid. An expression for $\mu_{\rm ion}$ can be found for the steady state situation, where the electric force on the ion, $\boldsymbol{F}_{\rm el} = Ze\boldsymbol{E}$, is balanced by the counteracting Stokes drag force, $\boldsymbol{F}_{\rm drag} = 6\pi\eta R\boldsymbol{v}_{\rm ep}$.

$$\mu_{\rm ion} \equiv \frac{Ze}{6\pi\eta R}.\tag{2.23}$$

Invoking Ohm's law for the electrical current density, $\mathbf{i} = \sigma \mathbf{E}$, the conductivity σ of the solution can be expressed by the ionic mobility μ and the concentration of ions c_i [16],

$$\sigma = Ze c_i \mu_{\text{ion}}.\tag{2.24}$$

In Table 2.2 table values for two common salt solutions are listed.

2.4.1 Nernst–Planck equation

The Nernst-Planck equation is the transport equation in electrohydrodynamics governing the total movement of electrically charged particles, i.e., ions, in a liquid system. The electrical particle current density j arises from gradients in the external applied fields of pressure p density c and potential ϕ . These contributions are assumed to superpose linearly, a valid approximation for dilute solutions regarding the terms of electromigration and diffusion [12].

$$\boldsymbol{j}_i \equiv -D_i \boldsymbol{\nabla} c_i + c_i \boldsymbol{v} - \mu_i c_i \boldsymbol{\nabla} \phi.$$
(2.25)

The first term on the right hand side is recognized as Fick's first law of diffusion, Eq. (2.6), arising from spatial variations of the ionic concentration. The second term expresses the

	0.1 mM	$1\mathrm{mM}$	$10\mathrm{mM}$	$0.1\mathrm{M}$
KCl σ [10 ⁻³ S/m]	1.4986	14.695	141.27	1289.6
NaCl σ [10 ⁻³ S/m]	1.2645	12.374	118.51	1067.4

Table 2.2: Table values for conductances of KCl and NaCl in different aqueous solutions at 25°C.

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particle flow due to convection, which can also be interpreted as a flow originating from external applied pressure differences. The electromigration is contained in the last term, since the electrical force on the ions depends on the applied electrical field expressed through the gradient of the electrostatic potential, $\boldsymbol{E} = -\boldsymbol{\nabla}\phi$. The index *i* emphasizes that the equation governs the transport of a single species in the liquid solution.

2.4.2 Electric double layer

In the following it is investigated how an electrolyte behaves in the region nearby a solid, which could for instance be the wall of a channel confining a liquid.

The total system will stay charge neutral, however due to chemical reactions between the solid and the electrolyte a local transfer of charge takes place, dependent on the specific solids and liquids in the system. In the electrolyte nearby the charged wall there will be an excess of counterions (charged opposite the wall) relative to coions, and far away from the solid surface the concentrations of differently charged ions are equivalent leaving the electrolyte neutral. This concentration surplus of counterions distributes from the wall into the liquid due to random thermal motion of the ions. A diffusion force counterbalances the electrical force on the ions resulting in a limited layer of predominantly counterions near the wall. The shielding of the charged wall, though, will not be perfect, given that the outermost ions of the layer have thermal energy to escape the electrostatic force of the wall.

As indicated at Fig. 2.3a the charged layer is divided into two parts dependent on wether the ions are mobile or not. The Stern layer has a thickness of approximately a hydrated ion radius and consists of counterions sticking to the surface in a mono layer due to the strong electrical forces [12]. The mobile layer, that may be influenced by an external applied electrical field, is termed the Debye layer and have a width of the order 10 nm, depending on several parameters such as electrolyte concentration and ion valences. The potential of the electrolyte is defined relative to a zero value of the neutral electrolyte in bulk far from the solid. At the shear interface screening by the Stern layer reduces the wall potential to another value designated the zeta-potential having a typical value in the range $\zeta \simeq 0 - 200 \,\mathrm{mV}$.

The ionic distributions $c_{\pm}(\mathbf{r})$ and the electrostatic potential $\phi(\mathbf{r})$ nearby the charged wall may in the continuum approximation be estimated from the chemical potential of the electrolyte, Eq. (2.11), including also the energy of the potential [16],

$$\mu_{\pm}(\boldsymbol{r}) = \mu_0 + k_{\rm B}T \,\ln\left(\frac{c_{\pm}(\boldsymbol{r})}{c_0}\right) \pm Ze\phi(\boldsymbol{r}). \tag{2.26}$$

In this case it is assumed that the electrolyte is symmetric containing two kinds of ions with equal and opposite valences $\pm Z$ and equal ionic concentrations c_0 in bulk. Also the reference chemical potentials are the same μ_0 .

For a system in thermodynamic equilibrium the chemical potential is constant everywhere, implying a zero gradient, $\nabla \mu_{\pm}(\mathbf{r}) = 0$. Eq. (2.26) now leads to

$$0 = k_{\rm B}T \,\boldsymbol{\nabla} \ln\left(c_{\pm}(\boldsymbol{r})\right) \pm Z e \boldsymbol{\nabla} \phi(\boldsymbol{r}). \tag{2.27}$$



Figure 2.3: An electrolyte (light gray area) in contact with a solid wall (dark gray area). a) Shows how the charged double layer near the wall is divided into an immobile Stern layer of thickness sand a mobile Debye layer of thickness $\lambda_{\rm D}$. b) A plot of the potential ϕ as a function of distance xfrom the wall, Eq. (2.33). C) Shows the corresponding ionic particle densities c_{\pm} as a function of distance x from the wall, Eq. (2.35). [16].

Integrating this equation and using the boundary conditions of the electrostatic potential and ionic concentrations far away from the solid, $c_{\pm}(\infty) = c_0$ and $\phi(\infty) = 0$, gives the following concentration functions,

$$c_{\pm}(\mathbf{r}) = c_0 \exp\left(\mp \frac{Ze}{k_{\rm B}T} \phi(\mathbf{r})\right).$$
(2.28)

Eq. (2.28) leads directly to the liquid charge distribution, since $\rho_{\rm el} = Ze(c_+ - c_-)$. An equation for the electrostatic potential can then be written utilizing the Poisson equation, Eq. (2.22), and the result is the Poisson–Boltzmann equation for the electrical potential

$$\nabla^2 \phi(\boldsymbol{r}) = \frac{2 Ze c_0}{\epsilon} \sinh\left(\frac{Ze}{k_{\rm B}T} \phi(\boldsymbol{r})\right). \tag{2.29}$$

A few analytical solutions of the above equation exist, but in general the equation has to be solved numerically [16].

Debye-Hückel limit

In the Debye–Hückel approximation a much simpler form of Eq. (2.29) appears, and this can be used to get a good indication of the actual solution form. The approximation is valid when the thermal energy of the system is much larger than the electrical energy, i.e. $Ze\zeta \ll k_bT$. Operating in this limit a Taylor expansion of the exponential functions in Eq. (2.28) is possible. Expanding to the first order, the ionic concentrations can be written as

$$c_{\pm}(\boldsymbol{r}) = c_0 \left(1 \mp \frac{Ze}{k_{\rm B}T} \,\phi(\boldsymbol{r}) \right), \qquad (2.30)$$

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which leads to a charge distribution linear in the potential,

$$\rho_{\rm el}(\mathbf{r}) = Ze(c_+(\mathbf{r}) - c_-(\mathbf{r})) = -\frac{2(Ze)^2 c_0}{k_{\rm B}T} \phi(\mathbf{r}).$$
(2.31)

Inserting this into the Poisson equation now results in a second order ordinary differential equation,

$$\nabla^2 \phi(\mathbf{r}) = \frac{2 \, (Ze)^2 c_0}{k_{\rm B} T \epsilon} \, \phi(\mathbf{r}). \tag{2.32}$$

If the wall is infinite and situated in the yz-plane with the electrolyte occupying the half-infinite space of x > 0, the ionic distributions will only depend on the distance x from the solid, resulting in a one dimensional equation. Since the width of the Stern layer is much smaller than the Debye layer thickness, the potential is assumed to take the value ζ at the wall, x = 0. Utilizing this boundary condition, the solution of Eq. (2.32) becomes the exponential function

$$\phi(x) = \zeta \exp\left(-\frac{x}{\lambda_{\rm D}}\right). \tag{2.33}$$

Here the characteristic length, named the Debye length, of the mobile Debye-layer has been introduced:

$$\lambda_{\rm D} \equiv \sqrt{\frac{\epsilon k_{\rm B} T}{2 \, (Ze)^2 \, c_0}}.\tag{2.34}$$

From Eqs. (2.30) and (2.31) the ionic concentration distributions and the charge distribution are now directly given as

$$c_{\pm}(\boldsymbol{r}) = c_0 \left[1 \mp \frac{Ze\zeta}{k_{\rm B}T} \exp\left(-\frac{x}{\lambda_{\rm D}}\right) \right], \qquad (2.35)$$

and

$$\rho(\mathbf{r}) = -\frac{\epsilon\zeta}{\lambda_{\rm D}^2} \exp\left(-\frac{x}{\lambda_{\rm D}}\right). \tag{2.36}$$

The potential and ionic distributions are shown at Fig. 2.3.

2.4.3 DC electroosmosis

Proceeding in the picture described above, where a solid channel wall is in contact with an electrolyte, a voltage difference is now applied over the ends of the channel. The ions in the mobile Debye layer are then attracted to the electrode of opposite charge dragging the charge neutral liquid in the same direction. Due to viscous forces the liquid will reach a final, steady state velocity called the electroosmotic velocity. In general electroosmosis is just defined as the movement of liquid relative to a charged stationary surface induced by an electric field [16, 12].

In the case of electroosmotic flow the Navier-Stokes equation, Eq. (2.4), contains a bodyforce $\rho_{\rm el} \boldsymbol{E}_{\rm ext} = -\rho_{\rm el} \boldsymbol{\nabla} \phi_{\rm ext}$ on the chargedensity $\rho_{\rm el}$ in the liquid.

$$\rho \left[\partial_t \boldsymbol{v} + (\boldsymbol{v} \cdot \boldsymbol{\nabla}) \boldsymbol{v} \right] = -\boldsymbol{\nabla} p + \eta \nabla^2 \boldsymbol{v} - \rho_{\rm el} \boldsymbol{\nabla} \phi_{\rm ext}.$$
(2.37)

Reasoning as in the previous section, the equation is quite easily solved in particular symmetric cases, for example nearby a wall. It is assumed that the ζ potential is constant along the wall, and that the external applied electric field is homogenous along the negative x-axis parallel to the wall, $\mathbf{E}_{\text{ext}} = -\mathbf{E} \mathbf{e}_x$. The velocity will then be directed in the x-direction only dependent on the coordinate y orthogonal to the wall, that is $\mathbf{v}(\mathbf{r}) = v_x(y)\mathbf{e}_x$. Furthermore the Debye length λ_{D} is supposed to be much smaller than possible channel dimensions. The equation is treated in the steady state situation and owing to the geometry of the velocity field the nonlinear inertia term becomes zero. If no external pressure difference is applied, and Poissons equation, Eq. (2.22), is used to express the charge density by the potential, Eq. (2.33), the Navier-Stokes equation takes the following one dimensional form:

$$0 = \eta \,\partial_y^2 v_x(y) + \left[\epsilon \,\partial_y^2 \phi(y)\right] E. \tag{2.38}$$

Utilizing the boundary conditions of an infinite wall, $\phi = \zeta$ when u = 0 and $\partial_y v_x = \partial_y \phi = 0$ for $y \to \infty$, an expression for the electroosmotic velocity appears, known as the Helmholtz-Smoluchowski equation [12]:

$$v_{\rm eo} \equiv \frac{\epsilon \zeta}{\eta} E. \tag{2.39}$$

If instead the boundary conditions of two infinite parallel plates are utilized, that is the no-slip condition at the channel walls $y = \pm h/2$ and zero potential between the plates, the following solution is obtained [16]. The velocity profile is also shown at Fig. 2.4.

$$v_x(y) = \left(1 - \frac{\cosh\left(\frac{y}{\lambda_d}\right)}{\cosh\left(\frac{h}{2\lambda_d}\right)}\right) v_{\rm eo}.$$
 (2.40)

The prefactor in Eq. (2.39) has for water an approximate value of $\epsilon \zeta /\eta \simeq 7 \times 10^{-8} \text{ m}^2/(\text{Vs})$, and for an *E*-field of around E = 100 V the EO-velocity will have an approximate value of $v_{\text{eo}} \simeq 7 \,\mu\text{m/s}$. Compared to microchip distances in the order of a few millimeters this velocity is very small, and though the electric field could be increased there is also a problem due to electrolysis of the water. Filters are demanded to keep bubbles out of the system, and even for high voltages the velocities do not become impressively high.



Figure 2.4: Velocity profile of electroosmotic flow between two infinite parallel plates as given by, Eq. (2.40). The profile is only position dependent within the mobile Debye layer at the walls while it takes the constant value $v_{\rm eo}$ between the plates.
Chapter 3

Modelling

The pump fabricated in the present project is based on the principle of induced-charge electrolytic flow, which involves the physics of electroosmosis outlined in Section 2.4. Inducedcharge flow does not necessarily involve charge transfer between the electrolyte and the electrodes, but is instead generated by an externally applied voltage. Electrodes in the bottom of a channel filled with electrolyte are biased with an external AC potential, which couples capacitively to the electrolyte and thereby causes liquid motion. An example of such an electrode array is shown in Fig. 3.1.

If the electrode array consists of spatially symmetric electrodes, there will be no resulting flow of the liquid across the electrodes, since the time average of the fluid motion is zero. However, if the symmetry is broken, either by variation of the electrode widths or by altering the capacitive coupling to the electrolyte for some of the electrodes, a net flow may be generated.

In this chapter, models of the electrodynamics and hydrodynamics behind the liquid motion are presented. An analytical model for an electrolyte above a symmetric electrode array is summarized to show the complexity of the liquid flow patterns. Since the analytical results only apply in low voltage regimes and include other simplifications, a few numerically obtained curves relating to the performed measurements are also presented. In these models the electrolyte is assumed to contain ions of equal and opposite valences with identical diffusivities. In order to examine the effect of dissimilar ions, a one dimensional analysis of a simple two-electrode system is carried out for such an electrolyte. This is done in the last section. First a pure electrical equivalent circuit for the fabricated electrode array is presented.



Figure 3.1: Small section of an electrode array with the microfluidic channel indicated as a red area. The electrode arrays have translation periods of $50 - 100 \,\mu\text{m}$. The array has been fabricated during this project.

3.1 Equivalent circuit

The electrodes shown in Fig. 3.1 corresponds to the chosen geometry in the fabricated micropump chip. The electrode array consists of alternating electrode widths and correspondingly alternating gaps, in order to break the symmetry. Thus, an array has a number of translation periods (typically 160-312) each containing a pair of electrodes and a pair of gabs. The narrow electrodes are biased with an AC voltage $V_{\text{ext}} = V_0 \sin(\omega t)$ and the wide electrodes are grounded. A double layer forms in the vicinity of the electrodes in order to screen the electrical field. These layers may be modelled as two separate capacitors coupled in series between the electrode conductor and the bulk electrolyte. The Debye layer capacitance C_{D} is defined on basis of the Debye length λ_{D} , and the intrinsic surface capacitance C_s , which could model the Stern layer or an intensionally grown surface oxide, depends on the width d of this layer. The area specific capacitances are given by [2]

$$C_s \equiv \frac{\epsilon_s}{d}, \qquad C_{\rm D} \equiv \frac{\epsilon}{\lambda_{\rm D}}.$$
 (3.1)

A series coupling of the above capacitors leads to the following resulting area specific capacitance of the entire double layer:

$$C_0 \equiv \left(C_s^{-1} + C_{\rm D}^{-1}\right)^{-1}.$$
(3.2)

Multiplying with the electrode area leads to the absolute double layer capacitance for each of the electrodes. These are denoted C_w and C_n for the wide and narrow electrodes, respectively.

The bulk electrolyte between two adjacent electrodes may be approximated with a resistor corresponding to the electrolytic resistance of a liquid cube between these electrodes. The length of the resistor-cube is given by the electrode spacing l_{gap} , and the cross sectional area is specified by the channel width w multiplied with the part of the channel height H occupied by electrical field lines terminating on the adjacent electrodes.

$$R_{\rm gap} \sim \frac{1}{\sigma} \frac{\rm length}{\rm area} \sim \frac{l_{\rm gap}}{\sigma w H} \sim \frac{3}{\sigma w},$$
 (3.3)

where σ is the conductivity of the electrolyte in the channel. The last expression is based on the assumption that the electrical field lines spread approximately 1/3 of the electrode spacing into the bulk electrolyte, i.e. $H \sim l_{\rm gap}/3$. It should be noted that the channel is sufficiently high to support this approximation. Thus, both the large and the small gap resistances R_l and R_s are approximated with the same value, $R_l \sim R_s \sim R_{\rm gap}$.

The resistance of the electrodes should also be included in the equivalent circuit. Since the current decreases along the electrode, only half of the electrode length is used in the approximation. The resistances of the narrow and wide electrodes are denoted R_n and R_w , respectively. A wire resistance is given by $R \sim \rho \text{length}/\text{area}$, where ρ is the resistivity of the metal.

An equivalent circuit consisting of the above mentioned components is sketched in Fig. 3.2. Each translation period is modelled by the same sub-diagram, which is then repeated to approximate the entire electrode array. The wires marked with an asterisk are



Figure 3.2: An overview of the electrical diagram approximation of an electrode array with alternating gaps and electrode widths covered with an electrolyte in a channel. A translation period of the electrode array is modelled by the black outlined part in the equivalent circuit. C_n and C_w represent the double layer capacitances for the narrow and wide electrodes, respectively, while R_n and R_w denote the corresponding electrode resistances. The electrolytic resistances between adjacent electrodes are modelled by R_l and R_s for the large and small gaps, respectively. The asterisk marked points are equipotential and connecting them does not change the circuit.



Figure 3.3: An equivalent diagram corresponding to one translation period in the electrode array. The electrolytic resistances between two electrodes are approximated with the same value $R_{\rm gap}$. Adjacent electrodes gives rise to an extra small capacitor C_{∞} in the diagram, and the contact wires leading to the electrode array adds a resistance $R_{\rm pad}$ to the equivalent circuit.

equipotential, since all capacitors connected to the same through wire are equal. Consequently, the sub-diagram outlined in black may be drawn as shown in figure Fig. 3.3. In this diagram an extra capacitor C_{∞} has been added to approximate the capacitive effect between adjacent electrodes. This small capacitor is of importance in the high frequency regime, where the ions in the electrolyte no longer have time to form the double layer. C_{∞} is a parallel coupling between each of the two capacitors within one translation period in the electrolyte filled channel. Additionally, the glass substrate provides a capacitive effect, which is also coupled in parallel and included in C_{∞} . Capacitances are estimated as $C \sim \epsilon$ area/length.

Finally, it is noted that additional resistances in contact pads and wires outside the electrode array, referred to as R_{pad} , are coupled in series with the entire array. If an electrode array consists of p translation periods, the total impedance is given by

$$Z = 2R_{\text{pad}} + \frac{1}{p} \left\{ R_w + R_n + \left[\left(\frac{R_{\text{gap}}}{2} + \frac{1}{i\omega C_n} + \frac{1}{i\omega C_w} \right)^{-1} + i\omega C_\infty \right]^{-1} \right\}.$$
 (3.4)

Plots of the absolute impedance and corresponding phase are seen in Fig. 3.4. The plots are based on the geometry of the fabricated micropumps outlined in Chapter 7. It should be noted that the impedance only in this simplified model tends to infinity for $\omega \to 0$. For the real system, electrode reactions occur in the DC limit allowing a small current to flow. However, the resistance experienced by this Faradaic current from the electrode into the Debye layer is very high for low voltages and has not been included [4].



Figure 3.4: The equivalent impedance of an electrode array given by Eq. (3.4). In a) the absolute impedance value is plottet as a function of angular frequency, and b) shows the corresponding phase for the same frequency interval. The values inserted in Eq. (3.4) are outlined in Chapter 7 and matches the fabricated microchips.

Returning to the double layer capacitance C_0 it should be observed that the voltage regime of the impedance measurement is important for the estimate. In the Debye– Hückel limit, i.e. low voltage regime, the Debye layer is rather thick, resulting in a Debye capacitance much smaller than the intrinsic surface capacitance, see Eq. (3.1). Since, the double layer capacitances are coupled in series, $1/C_s$ might be neglected in this regime. Conversely, the Debye layer becomes very narrow in the high voltage regime, and thus the entire voltage drop will be across the intrinsic surface layer. Thus, in the high voltage regime, the reciprocal Debye layer capacitance $1/C_D$ can be neglected. These relations between C_s and C_D leaves a possibility to directly measure the capacitances.

3.2 Induced-charge electroosmotic pump

The pumping and mixing of an electrolyte above an asymmetric electrode array have been theoretically investigated. Analytical models in the Debye-Hückel regime confirm numerically obtained flow patterns of high complexity. In this section, a model of the liquid motion above the electrodes is shortly described, and a few numerical results regarding the fluid velocity are presented.

3.2.1 Symmetric electrodes

The basic motion of an electrolyte in the vicinity of a symmetric electrode array exposed to an alternating, time dependent voltage has been studied by Mortensen *et al.* [2]. The model presented in this article is summarized in the following, giving an impression of the complexity behind the fluid pattern and resulting pumping effect.



Figure 3.5: The studied system modelling a symmetric electrode array in an electrolyte. The electrodes are approximated by a spatially periodic potential $V_{\text{ext}}(y,t)$ at x = -d. The semi infinite conductor is covered with an insulating layer of thickness d above which a binary, symmetric electrolyte fills the remaining half-space. Due to the externally applied potential a Debye layer forms at the insulator-electrolyte interface. [2]

The studied geometry is shown in Fig. 3.5 and consists of a conductor covered with an insulator, which is in contact with an electrolyte containing two kinds of ions with equal diffusivity D and opposite valences $\pm Z$. The electrolyte occupies the half space x > 0, the insulating plane has a thickness of d, and the conductor fills out the remaining half space, x < -d. The symmetric electrode array is modelled as a periodically modulated potential $V_{\text{ext}}(y, t)$ applied to the conductor surface located at x = -d. Due to the externally applied potential, a Debye layer forms in the vicinity of the insulating layer, which could be an oxide grown on the electrode surface or simply the Stern layer. Full translation invariance is assumed in the z-direction, thus field variations only occurs in the x, y plane.

Five different fields are considered in the electrolyte; the electrical potential $\phi(\mathbf{r}, t)$, the ionic particle densities $c_{\pm}(\mathbf{r}, t)$, the particle current densities $\mathbf{j}_{\pm}(\mathbf{r}, t)$, the liquid velocity field $\mathbf{v}(\mathbf{r}, t)$ and the pressure $p(\mathbf{r}, t)$. In the presentation below of the equations governing these fields, the dependence (\mathbf{r}, t) has been suppressed. The Poisson equation, Eq. (2.22),

relates the ionic particle density with the potential in the liquid,

$$\nabla^2 \phi(\mathbf{r}, t) = -\frac{Ze}{\epsilon} \left(c_+ - c_- \right). \tag{3.5}$$

Neglecting chemical reactions in the system, the particle density is coupled to particle current density via the continuity equation, Eq. (2.1),

$$\partial_t c_{\pm} = -\boldsymbol{\nabla} \cdot \boldsymbol{j}_{\pm}. \tag{3.6}$$

Linearity is assumed between the different contributions to the particle current density, which is then governed by the Nernst–Planck equation, Eq. (2.25),

$$\boldsymbol{j}_{\pm} = -D\boldsymbol{\nabla}c_{\pm} + c_{\pm}\boldsymbol{v} \mp \mu c_{\pm}\boldsymbol{\nabla}\phi.$$
(3.7)

It is noted that the ionic mobility μ is coupled to the diffusivity D and electric conductivity σ through the Einstein relations $D = (k_{\rm B}T/Ze)\mu$ and $\sigma_{\pm} = Zec_{\pm}\mu$.

The Navier–Stokes equation, Eq. (2.4), connects the pressure field and fluid velocity with the potential and ionic particle densities,

$$\rho\left(\left[\partial_t \boldsymbol{v} + (\boldsymbol{v} \cdot \boldsymbol{\nabla})\boldsymbol{v}\right] = -\boldsymbol{\nabla}p + \eta \nabla^2 \boldsymbol{v} - Ze(c_+ - c_-)\boldsymbol{\nabla}\phi_{\text{ext}}.$$
(3.8)

Finally the assumed incompressibility of the liquid electrolyte is expressed by Eq. (2.2),

$$\boldsymbol{\nabla} \cdot \boldsymbol{v} = 0. \tag{3.9}$$

The boundary conditions of the problem are specified in accordance with the geometry of Fig. 3.5. Supposing that the intrinsic ζ potential at the insulator surface has been compensated by a corresponding DC shift added to the applied AC potential, the surface potential is entirely given by the external applied AC voltage. The spatial modulation along the surface has a period of $2\pi/q$, and the voltage with amplitude V_0 is driven at the angular frequency ω . In the bulk electrolyte far from the insulating layer, the potential is assumed to be zero.

$$\phi(\mathbf{r},t)|_{x=0} = V_{\text{ext}}(y,t) = V_0 \cos(qy) e^{i\omega t}, \qquad (3.10a)$$

$$\phi(\boldsymbol{r},t)|_{\boldsymbol{x}=\boldsymbol{\infty}} = 0. \tag{3.10b}$$

Considering the ionic particle current densities, the normal component at the insulator surface must be zero. The convection term $(c_{\pm}\boldsymbol{v})$ of Eq. (3.7) is neglected at the surface due to the no-slip boundary condition $\boldsymbol{v}(\boldsymbol{r},t)|_{x=0}=0$, resulting in the following boundary conditions for the ionic current densities,

$$0 = \partial_x c_{\pm}(\boldsymbol{r}, t)|_{x=0} \pm \frac{Ze}{k_{\rm B}T} c_{\pm}(\boldsymbol{r}, t) \,\partial_x \phi(\boldsymbol{r}, t)|_{x=0}.$$
(3.11)

The last condition necessary to solve the problem is specified for the ionic particle density. Charge neutrality is assumed in the bulk electrolyte, and since the ionic valences have the same absolute value, the particle concentrations of the two ions must be equivalent in bulk.

$$c_{\pm}(\boldsymbol{r},t)|_{\boldsymbol{x}=\boldsymbol{\infty}} = c_0 \tag{3.12}$$

The solving of the equations starts with an elimination of the current densities by insertion of Eq. (3.7) into Eq. (3.6) resulting in the continuity equation

$$\partial_t c_{\pm} = D\nabla^2 c_{\pm} - (\boldsymbol{\nabla} c_{\pm}) \cdot \boldsymbol{v} \pm \mu \boldsymbol{\nabla} \cdot (c_{\pm} \boldsymbol{\nabla} \phi).$$
(3.13)

An analytical solution of the above equation is enabled by the introduction of a linearized ionic particle density. As stated in the boundary conditions Eq. (3.12), the ionic densities have the same value ρ_0 far from the insulator surface in the bulk electrolyte, leading to

$$c_{\pm}(\boldsymbol{r},t) = c_0 + \delta c_{\pm}(\boldsymbol{r},t), \qquad \lim_{x \to \infty} \delta c_{\pm}(\boldsymbol{r},t) = 0.$$
(3.14)

In the Debye-Hückel limit, where the thermal voltage $(k_{\rm B}T/Ze \sim 25 \text{ mV})$ is much larger than the applied voltage V_0 , the particle density deviation is small, $|\delta \rho_{\pm}| \ll \rho_0$. Consequently, $\rho_{\pm} \nabla \phi$ may be substituted by $\rho_0 \nabla \phi$ in Eq. (3.13). Utilizing the Poisson equation, Eq. (3.5), to express $\nabla^2 \phi$ through the ionic particle densities, results in two coupled differential equations of c_+ and c_- . Forming the difference between these equations and utilizing the expression for the Debye length $\lambda_{\rm D}$, Eq. (2.34), gives rise to a second order partial differential equation,

$$\partial_t \nu = \left(D\nabla^2 - D \frac{1}{\lambda_D^2} - \boldsymbol{v} \cdot \boldsymbol{\nabla} \right) \nu, \qquad (3.15)$$

where the ionic particle density difference is termed $\nu \equiv c_{+} - c_{-} = \delta c_{+} - \delta c_{-}$.

Since the charge density only has a non-zero value within the Debye layer $(x \leq 3\lambda_{\rm D})$, this is the regime where Eq. (3.15) has to be solved. Due to the no-slip boundary condition, the convection term may be neglected in this regime, leading to

$$\partial_t \nu = \left(D\nabla^2 - D\frac{1}{\lambda_{\rm D}^2} \right) \nu. \tag{3.16}$$

Thus, diffusion dominates and the electrodynamics can be solved independently of the hydrodynamics. However, it should be noted that the hydrodynamics depends on the electrodynamics through the body force generated when the ions are affected by potential gradients.

The solution of Eq. (3.16) is inserted into the Poisson equation, Eq. (3.5), from which the potential field is determined. Utilizing the boundary conditions Eqs. (3.10) and (3.11)to determine the integration constants, the potential is given by [16]

$$\phi(x,y,t) = \frac{V_0}{\omega_{\rm D} + i\frac{\kappa}{q}\omega} \left(\omega_{\rm D}e^{-\kappa x} + i\frac{\kappa}{q}\omega e^{-qx}\right)\cos(qy)e^{i\omega t}, \qquad x > 0, \tag{3.17}$$

where

$$\kappa \equiv \frac{1}{\lambda_{\rm D}} \sqrt{1 + (q\lambda_{\rm D})^2 + i\frac{\omega}{\omega_{\rm D}}},\tag{3.18}$$

and the Debye frequency is defined as

$$\omega_{\rm D} \equiv \frac{D}{\lambda_{\rm D}^2}.\tag{3.19}$$

In the regime with a spatial modulation period much longer than all other length scales in the system, $q\lambda_{\rm D} \ll 1$ and $qd \ll 1$, and a driving frequency smaller than the Debye frequency, $\omega \ll \omega_{\rm D}$, the expression for κ , Eq. (3.18), is simplified to $\kappa \simeq 1/\lambda_{\rm D}$. This gives rise to the following expression for the potential in the bulk electrolyte [2].

$$\phi(x, y, t) = V_0 \frac{i\omega}{\omega^* + i\omega} e^{-qx} \cos(qy) e^{i\omega t}, \qquad x \gtrsim 3\lambda_{\rm D}, \tag{3.20}$$

where $\omega^* \equiv q \lambda_{\rm D} \omega_{\rm D}$ is the characteristic resonance frequency. Eq. (3.20) is depicted in Fig. 3.6.

The flow pattern in the electrolyte above the electrodes is determined through the Navier–Stokes equation, Eq. (3.8), where the body force is found as $\mathbf{f} = -Ze\nu\nabla\phi = -Ze\mathrm{Re}\{\nu\}\mathrm{Re}\{\nabla\phi\}$. The viscous term on the left-hand side of the equation dominates the inertial terms on the right-hand side when $\omega \ll \omega_{\mathrm{D}}$, thus the Navier–Stokes equation takes the form [16]

$$\mathbf{0} = -\boldsymbol{\nabla}p + \eta \nabla^2 \boldsymbol{v} + \boldsymbol{f}. \tag{3.21}$$

In the Debye layer $(0 < x \leq 3\lambda_{\rm D})$, the above equation is solved by separation of length scales. The body-force changes over a length scale q^{-1} in the *y*-direction, while the variation in the *x*-direction is much faster that is in the order $\lambda_{\rm D}$. Also the velocity components may be separated, since the shear flow close to the wall is much larger than the flow normal to the surface, where the no-slip boundary condition is applied, i.e. $v_x \sim 0$.

Solving for the velocity component in the y-direction gives

$$v_y(x,y) = v_s(y,t)\sin(2qy)\left(1 - e^{-x/\lambda_{\rm D}}\right), \qquad 0 < x \lesssim 3\lambda_{\rm D}.$$
 (3.22)

where a slip velocity $v_s(y, t)$, corresponding to the earlier defined EO slip velocity, Eq. (2.39), is introduced for the limit $v_y(\infty, y, t)$.

$$v_s(y,t) \equiv v_1 \, \frac{\cos(2\omega t + \psi)}{\frac{\omega}{\omega^*} + \frac{\omega^*}{\omega}} \, \sin(2qy), \qquad (3.23)$$

with

$$v_1 \equiv \frac{q\epsilon V_0^2}{4\eta}, \text{ and } \psi \equiv -\arctan\left(\frac{\omega}{2\omega^*} + \frac{\omega^*}{2\omega}\right)$$
 (3.24)

The velocity field in the Debye layer is depicted in Fig. 3.6.

In the bulk electrolyte for $x \gtrsim 3\lambda_{\rm D}$, the body force is absent and the Navier–Stokes equation only consists of two terms governing the viscosity and the pressure. The slip velocity v_s introduced above is used as boundary condition for the velocity field in this

regime. The resulting fields of pressure and velocity are given by [16]

$$v_x(x,y,t) = -v_1 \frac{\cos(2\omega t + \psi)}{\frac{\omega}{\omega^*} + \frac{\omega^*}{\omega}} e^{-2qx} 2qx \cos(2qy), \qquad (3.25)$$

$$v_y(x, y, t) = v_1 \frac{\cos(2\omega t + \psi)}{\frac{\omega}{\omega^*} + \frac{\omega^*}{\omega}} e^{-2qx} (1 - 2qx) \sin(2qy), \qquad (3.26)$$

$$p(x,y,t) = -4q\eta v_1 \frac{\cos(2\omega t + \psi)}{\frac{\omega}{\omega^*} + \frac{\omega^*}{\omega}} e^{-2qx} \cos(2qy).$$
(3.27)

Plots of the above fields are seen in Fig. 3.6.



Figure 3.6: The potential ϕ , pressure p and velocity field v. a) Plot of the potential amplitude as a function of qx and qy given by Eq. (3.20). b) The corresponding pressure field, Eq. (3.27). c) The velocity field in the bulk electrolyte at a time instant, Eqs. (3.25) and (3.26). d) The flow pattern in the Debye layer a the same instant of time, Eq. (3.22). Lines of constant velocity are drawn. [2]

3.2.2 Asymmetric electrodes

In the previous subsection it has been explained how fluid rolls are generated in an electrolyte above a spatial cosine varying potential. However, in the fabricated device, the electrodes are equipotential surfaces of finite size, spaced with insulating gaps. Such a geometry has been theoretically examined by Olesen *et al.* [4], and the following numerical results are extracted from this article.

An electrode array consists of narrow and wide electrodes biased with an AC voltage $V_{\text{ext}} = \pm V_0 \cos(\omega t)$, respectively. The electrodes are placed in a channel containing an electrolyte, which is charge neutral in bulk far from the conducting surfaces. The geometry of the problem is sketched in Fig. 3.7, and it should be noted that full symmetry is assumed in the third dimension, i.e. the problem is two dimensional. The externally applied voltage causes the formation of a Debye layer at the electrode surfaces that partially screens the electric field. In the vicinity of the electrode corners, the charge concentration is bigger

and the density of E-field lines larger, compared to the middle of the electrode. This gives rise to tangential electric fields in the Debye layer, which induce electroosmotic flow from the electrode corners towards the center. The boundary condition on the electrodes are thus based on the Helmholtz-Smoluchowsky slip velocity, Eq. (2.39).

$$u_s = -\frac{E_t \,\epsilon\,\zeta}{\mu},\tag{3.28}$$

where $E_t = -\partial_x \phi$ is the tangential field in the Debye layer. On the insulating walls between the electrodes, the no-slip boundary condition applies. Solving the Navier–Stokes equation for the fluid velocity field in the channel and applying the outlined boundary conditions, results in a complex flow pattern consisting of rolls above the electrode corners as indicated in Fig. 3.7.



Figure 3.7: The geometry analysed in the article of Olesen *et al.* [4], consisting of an asymmetric electrode array exposed to a symmetric electrolyte in a channel of infinite width. The electrode translation period is L in the x direction and the channel height is H along the y axis. A voltage difference of $2V_0 \cos(\omega t)$ is applied between the small and large electrodes. Due to tangential electric fields on the electrodes, electroosmotic flow is induced, resulting in fluid rolls above the electrode edges. In spite of this complex flow pattern, it may be shown by Fourier analysis of the total flow rate through the channel that on average, the flow is a simple Couette flow. This is indicated by arrows.

In spite of the complex fluid motion induced in the electrolyte, it is possible to treat the net pumping in a simpler way. A Fourier analysis of the total flow rate through the channel of height H, $\langle U \rangle = \int_0^H \langle u_x \rangle dy$, shows that the flow on average in time and space is a simple Couette flow [4]. The flow is driven by the slip velocity U averaged over the electrode surfaces. Assuming no back pressure, the flow rate is given by Eq. (2.14),

$$\langle Q \rangle = \frac{HU}{2}.\tag{3.29}$$

The Couette flow is indicated with arrows in Fig. 3.7. Consequently, the velocity is determined entirely from the solution to the electrical problem.

A linear analysis of the problem in the Debye–Hückel limit gives an impression of how the average fluid velocity through the channel depends on frequency of the applied voltage. This may be investigated assuming a vanishing Faradaic current from the electrodes into the Debye layer.

In the Debye layer, the charge is calculated as

$$q = -\frac{\epsilon}{\lambda_{\rm D}}\,\zeta = -C_{\rm D}\,\zeta,\tag{3.30}$$

and the potential drop across the entire double layer, from V_{ext} at the electrode to ϕ in the bulk electrolyte is given by

$$V_{\text{ext}} - \phi = \zeta - \frac{q}{C_s}.$$
(3.31)

Neglecting the Faradaic current from electrochemical reactions at the electrodes, the charging $\partial_t q$ of the Debye layer is entirely due to Ohmic current $\mathbf{i} = -\sigma \nabla \phi$ from the bulk electrolyte, where σ is the conductivity of the electrolyte:

$$\partial_t q = -\boldsymbol{n} \cdot \boldsymbol{i}, \tag{3.32}$$

where n is a unit normal vector directed away from the surface. Surface diffusion and migration of charge in the Debye layer is neglected.

In the bulk electrolyte, the charge continuity equation is utilized, $\nabla \cdot \mathbf{i} = 0$, leading to a Laplace problem for the potential. On the insulating walls between the electrodes and at the channel lid, the normal component of the current vanishes, leading to $\mathbf{n} \cdot \mathbf{i} = 0$.

The variables of the problem are rescaled in accordance with characteristic dimensions of the system and subsequently the equations are solved numerically. The resulting relation between the dimensionless angular frequency and the average fluid velocity above the electrodes is depicted in Fig. 3.8a. The characteristic frequency of the system is obtained from the Ohmic relaxation time τ_0 in the low voltage regime. τ_0 is the *RC* time of a simple circuit consisting of the area specific double layer capacitance C_0 (Eq. (3.2)) in series with the area specific bulk resistance $R_0 = l_0/\sigma$, where l_0 is the characteristic length of the system, corresponding to the smallest electrode gap of the array. Thus, $\tau_0 = R_0C_0$ and the angular frequency is rescaled as $\omega = \tau_0^{-1}\tilde{\omega}$. The tilde denotes dimensionless variables. Regarding the characteristic velocity u_0 , this is calculated from Eq. (3.28). Here the ζ potential is approximately $\zeta \sim V_0/(1-\delta)$, where $\delta = C_D/C_s$ denotes the relation between the double layer capacitances. The tangential electric field is of the size $E_t \sim V_0/l_0$. Inserting these expression into the formula of slip velocity results in an absolute characteristic velocity of $u_0 = \epsilon V_0^2/\mu l_0(1+\delta)$, thus, $\mathbf{u} = u_0\tilde{\mathbf{u}}$.

From Fig. 3.8a it is apparent, that an optimal driving frequency exist, $\tilde{\omega} = 1$, where the average fluid velocity at the electrodes is highest. This resonance frequency is caused by the ionic response on the voltage change. For very low frequencies, $\tilde{\omega} \ll 1$, the ions screens the electrical field completely, and no electroosmotic flow is induced, since the tangential *E*-field is absent. When the frequency becomes higher, $\tilde{\omega} \gg 1$, the ions are not fast enough to efficiently screen the applied voltage, thus there is no charge in the Debye layer to induce a flow. Fig. 3.8a is only valid in the Debye–Hückel limit that is for voltages much lower than the voltage necessary to obtain an experimental detectable net fluid velocity. Olesen *et al.* [4] has extended the solution of the problem to the nonlinear high voltage regime, and obtained numerical results for a symmetric monovalent electrolyte.

The potential drop across the double layer is still given by Eq. (3.31) and the current into the Debye layer is also unchanged Eq. (3.32) if the Faradaic currents also in this case are neglected. For a large surface potential, though, the charge in the Debye layer is different,

$$q = -\frac{\epsilon}{\lambda_{\rm D}} \frac{2k_{\rm B}T}{e} \sinh\left(\frac{Ze\zeta}{2k_{\rm B}T}\right). \tag{3.33}$$

Corresponding to the linear solution, the equations are rescaled and solved numerically. In Fig. 3.8b a contour plot of the average pumping velocity above the electrodes as a function of angular frequency and driving voltage is shown. The voltage is in this case rescaled by the thermal voltage of the system, $k_{\rm B}T/e$, leading to $V_0 = (k_{\rm B}T/e)\tilde{V}_0$. From the plot, it is apparent how the resonance frequency shifts towards lower frequencies when the applied voltage is increased. The Stern layer dominates the double layer capacitance and the resonance frequency is here $\tau_{\infty}^{-1} = \tau_0^{-1}/(1 + \delta^{-1})$. The shape of the curve remains almost the same compared to the low voltage regime, only the fluid velocity decreases slower when the frequency is increased above the resonance frequency.



Figure 3.8: The average fluid velocity \tilde{U} above the electrodes. a) The velocity as a function of driving frequency $\tilde{\omega}$ in the Debye–Hückel limit, i.e. low voltage regime, $V_0 \ll 25$ mV. Due to the relation between the driving frequency and the ionic response time a resonance peak occurs. The dashed line shows the tangent $\tilde{U} \propto \tilde{\omega}^2$. b) A contour plot of the velocity as a function of driving frequency and voltage \tilde{V}_0 . The solution is extended to the nonlinear regime, where $V_0 \gg 25$ mV, and a clear shift of the resonance peak towards lower frequencies is seen. This is indicated by the dashed line.

In the summarized article [4] a thorough investigation of the system geometry in relation to flow velocity has been performed. Regarding the channel height, a shift in the resonance frequency towards lower frequencies combined with a slightly increased flow velocity, has been observed for a confined geometry, i.e., when the height becomes small. This effect is relevant when the electrode period is at least twice the height of the channel, $L \gtrsim 2H$, which is not the case for the devices fabricated in the present project.

The relation between the electrode widths and spacings within a given translation period has also been considered to determine the geometry leading to the maximal fluid velocity. It was though concluded that rather big variations of the geometry do not imply significant changes in the velocity. However, the resonance frequency may differ by almost a factor of 2.

3.2.3 Parameters to be investigated

Parameters which would be relevant for further investigations are shortly summarized on basis of the reviewed articles.

As mentioned, a frequency shift is observed for confined geometries, and by variation of the channel height relative to the translation period of the electrode array, it would be interesting to investigate this effect. Furthermore, predictions about the generated flow velocities are based on electrode geometry and the externally applied voltage, thus it would be relevant to study how the fluid velocity responds to variations of these variables. Another parameter, which has an impact on both velocity and resonance frequency in the micropump system, is the electrolytic concentration. This parameter would be rather easy to vary.

Several of these parameters have previously been investigated, however, the channel height has for instance not been studied. Additionally, unexpected effects in connection with variation of the other parameters are unexplained and should still be attended. An example is the effect of flow generation in "reverse" direction. Large flow velocities have been observed, opposite the expected direction, when the voltages and frequencies become high [3].

Another problem, which has been reported, relates to the stability of the electrodes. During usage, the electrodes seems to be worn down and it would be desirable to protect the metal surface. In the summarized article about fluid rolls above a harmonic varying potential [2] an insulating layer has been applied above the potential. Regarding this layer as a protective electrode oxidation, it would be interesting to investigate how the flow generation is affected experimentally. Additionally, it has been suggested that a variation of this oxide thickness would be another possible way to create asymmetry in the system and generate flow [1]. This is also a prediction which should be further examined.

3.3 Asymmetric electrolyte

In the previous sections, it was assumed that the electrolyte above the electrode array was symmetric, i.e., the ions were supposed to have equal diffusivity and absolute valences. In this section an electrolyte containing dissimilar ions has been investigated analytically in a one dimensional problem. The liquid is confined between two infinitely wide parallel plates, across which a time dependent voltage difference is applied. This system is thought as a rough simplification of a two electrode system, which could for instance be two adjacent electrodes in the array of an induced charge electroosmotic pump. Most salts consists of ions which differs in size causing the diffusion constants to be unequal, see Eq. (2.12). Especially does biomolecules, $D \sim 10^{-11} \text{m}^2/\text{s}$, have a significantly lower diffusivity compared to small ions, $D \sim 2 \times 10^{-9} \text{m}^2/\text{s}$. Different valences are found when salts are diluted in water, CaCl₂ is an example consisting of Ca²⁺ ions and Cl⁻ ions. In the following such electrolytes are examined.

3.3.1 Debye layer

The electric double layer formed by an electrolyte in the vicinity of a solid wall has been introduced in Section 2.4.2. The potential ϕ and ionic concentrations c_{\pm} in the Debye layer, Eqs. (2.33) and (2.35), were calculated in the Debye–Hückel limit based on the assumption that the electrolyte was symmetric. As a first approach in the investigation of asymmetric electrolytes, a corresponding calculation is performed for a solution containing two kinds of ions with opposite and unequal valences $Z_{+} \neq Z_{-}$. For convenience the valence ratio $m \equiv Z_{+}/Z_{-}$ is introduced leading to the following notation $Z_{-} \equiv Z$ and thus $Z_{+} = mZ$.

The chemical potentials, Eq. (2.26), take the following form for the constituents of an asymmetric electrolyte yet having the same reference chemical potentials μ_0 .

$$\mu_{+}(\boldsymbol{r}) = \mu_{0} + k_{\mathrm{B}}T \ln\left(\frac{c_{+}(\boldsymbol{r})}{c_{0}}\right) + mZe\phi(\boldsymbol{r})$$
(3.34a)

$$\mu_{-}(\boldsymbol{r}) = \mu_{0} + k_{\mathrm{B}}T \ln\left(\frac{c_{-}(\boldsymbol{r})}{c_{0}}\right) - Ze\phi(\boldsymbol{r}).$$
(3.34b)

In thermodynamic equilibrium the chemical potentials are constant everywhere, implying zero gradients, $\nabla \mu_{\pm}(\mathbf{r}) = 0$. Inserting Eq. (3.34) gives

$$0 = k_{\rm B} T \, \boldsymbol{\nabla} \ln \left(c_+(\boldsymbol{r}) \right) + m Z e \boldsymbol{\nabla} \phi(\boldsymbol{r}) \tag{3.35a}$$

$$0 = k_{\rm B} T \, \boldsymbol{\nabla} \ln \left(c_{-}(\boldsymbol{r}) \right) - Z e \boldsymbol{\nabla} \phi(\boldsymbol{r}). \tag{3.35b}$$

Integrating Eq. (3.35) and implementing the boundary conditions for the electrostatic potential and ionic concentrations far from the solid in the bulk electrolyte, leads to the ionic concentration functions. In correspondence with the symmetric case, the bulk electrolyte is assumed to be charge neutral and, consequently, the ionic concentrations must be related as $c_{-}^{\infty}/c_{+}^{\infty} = m$ in order to compensate the valence difference. The boundary conditions can thus be written $c_{+}^{\infty} \equiv c_0$ and $c_{-}^{\infty} = mc_0$. The potential in the bulk electrolyte is unchanged $\phi(\infty) = 0$, and the ionic concentration functions are then given by

$$c_{+}(\boldsymbol{r}) = c_{0} \exp\left(-\frac{mZe}{k_{\rm B}T}\,\phi(\boldsymbol{r})\right) \tag{3.36a}$$

$$c_{-}(\boldsymbol{r}) = m c_{0} \exp\left(\frac{Ze}{k_{\rm B}T} \phi(\boldsymbol{r})\right).$$
(3.36b)

Restricting further calculations to the Debye–Hückel limit facilitates a Taylor expansion of the exponential functions, as in the case of a symmetric electrolyte. The charge

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distribution in the liquid then takes the form

$$\rho_{\rm el}(\mathbf{r}) = mZec_{+}(\mathbf{r}) - Zec_{-}(\mathbf{r})$$

$$= mZec_{0} \left[1 - \frac{mZe}{k_{\rm B}T} \phi(\mathbf{r}) - \left(1 + \frac{Ze}{k_{\rm B}T} \phi(\mathbf{r}) \right) \right]$$

$$= -\frac{(Ze)^{2}c_{0}}{k_{\rm B}T} m(m+1) \phi(\mathbf{r}). \qquad (3.37)$$

Inserting this into the Poisson equation (Eq. (2.22)), the differential equation for the potential can be written as

$$\nabla^2 \phi(\mathbf{r}) = \frac{(Ze)^2 c_0}{k_{\rm B} T\epsilon} m(m+1) \,\phi(\mathbf{r}). \tag{3.38}$$

In accordance with the calculation for a symmetric electrolytic solution, the wall is also in this case assumed to be infinite in the yz-plane with the electrolyte occupying the halfinfinite space x > 0. Eq. (3.38) thus becomes one dimensional. Employing the boundary condition $\phi(0) = \zeta$ results in the exponential function also obtained in the symmetric case (Eq. (2.33)), however, the asymmetric electrolyte gives rise to a different Debye length, dependent on the valence ratio of the ions m.

$$\phi(x) = \zeta \, e^{-x/\lambda_{\mathrm{D,a}}},\tag{3.39}$$

where

$$\lambda_{\rm D,a} \equiv \sqrt{\frac{\epsilon k_{\rm B} T}{(Ze)^2 c_0} \frac{1}{m(m+1)}} \,. \tag{3.40}$$

Substituting c_{-}^{∞} , c_{+}^{∞} , Z_{-} and Z_{+} for m, c_{0} and Z, and utilizing that $c_{+}^{\infty}eZ_{+} = c_{-}^{\infty}eZ_{-} = \rho_{0}$, where ρ_{0} is the charge density in the bulk electrolyte for either of the two ions, results in the following expression for the Debye length:

$$\lambda_{\rm D,a} = \sqrt{\frac{\epsilon k_{\rm B} T}{e^2}} \frac{1}{c_+^{\infty} Z_+^2 + c_-^{\infty} Z_-^2}$$
$$= \sqrt{\frac{\epsilon k_{\rm B} T}{e}} \frac{1}{\rho_0 (Z_+ + Z_-)}.$$
(3.41)

It is noted, that for a symmetric electrolyte with $Z_+ = Z_-$, the expression of Eq. (2.34) is obtained.

From Eq. (3.36) the ionic concentrations are given by

$$c_{+}(\mathbf{r}) = c_{+}^{\infty} \left[1 - \frac{Z_{+}e\zeta}{k_{\rm B}T} e^{-x/\lambda_{\rm D,a}} \right]$$
 (3.42a)

$$c_{-}(\mathbf{r}) = c_{-}^{\infty} \left[1 + \frac{Z_{-}e\zeta}{k_{\rm B}T} e^{-x/\lambda_{\rm D,a}} \right],$$
 (3.42b)

and the charge distribution becomes equal to Eq. (2.36) with the Debye length of Eq. (3.41) inserted.

$$\rho(\mathbf{r}) = -\frac{\epsilon \zeta}{\lambda_{\mathrm{D,a}}^2} e^{-x/\lambda_{\mathrm{D,a}}}.$$
(3.43)

3.3.2 Parallel plate capacitor

In this section the geometry has been extended to comprise two infinite parallel plates bounding an asymmetric electrolyte. The plates are oppositely charged by an external applied potential difference, which causes Debye layers to form in the vicinity of both walls. If the plates are positioned in the yz-plane with the distance L on the x-axis, the field variations in the electrolyte are only dependent on the x-coordinate due to symmetry, i.e. the problem is one dimensional. The geometry is sketched in Fig. 3.9.



Figure 3.9: Two infinitely wide parallel conducting plates bounding an asymmetric electrolyte. The plates are oppositely charged with an AC signal of $V_{\text{ext}} = \pm V_0 e^{i\omega t}$, respectively. In this geometry, the problem of calculating the potential variation and ionic distributions in the electrolyte becomes 1D.

Below, the ionic distributions $c_{\pm}(x,t)$ and potential variation $\phi(x,t)$ between the plates has been investigated analytically. For simplicity the fields in the electrolyte are calculated for a time independent potential difference as a first approach. Afterwards, the external applied potential difference between the plates is assumed to be a harmonic oscillating function of time. This leads to ionic distributions, that are dependent on the relation between applied frequency and ionic diffusivity, i.e. the ionic respond to the changing potential. A simpler calculation for a fully symmetric electrolyte is first carried out, and subsequently the solution for an asymmetric electrolyte is presented.

The physics is governed by the same equations as outlined in Section 3.2, except that the ionic diffusivity and mobility differs for the two oppositely charged ions. Furthermore, the ionic particle densities $c_{\pm}(x,t)$ are replaced by the charge densities $\pm \rho_{\pm}(x,t) = \pm c_{\pm}(x,t)Z_{\pm}e$. In the following all signs are noted explicitly, and (x,t) is suppressed for clarity. The potential is coupled to the charge densities through the Poisson equation,

$$\nabla^2 \phi(\mathbf{r}, t) = -\frac{1}{\epsilon} \left(\rho_+ - \rho_- \right) = -\frac{1}{\epsilon} \left(\delta \rho_+ - \delta \rho_- \right). \tag{3.44}$$

The continuity equation relates the charge density to the current density i_{\pm} as

$$\partial_t \rho_{\pm} = -\boldsymbol{\nabla} \cdot \boldsymbol{i}_{\pm},\tag{3.45}$$

and finally the Nernst–Planck equation describes the origin of current densities from concentration gradients, convection and E-fields,

$$\boldsymbol{i}_{\pm} = -D_{\pm}\boldsymbol{\nabla}\rho_{\pm} + \rho_{\pm}\boldsymbol{v} \mp \mu_{\pm}\rho_{\pm}\boldsymbol{\nabla}\phi.$$
(3.46)

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In this capacitor system the fluid velocity is very low, since motion is confined to the Debye layer, where ions may be affected by an oscillating wall potential, and there is no potential variations along the wall. Consequently, the convection term $\rho_{\pm} v$ has been neglected in the Nernst–Planck equation. Only the diffusive regime is considered and the electrodynamics of the system may be solved independently of the hydrodynamics, thus the Navier–Stokes equation is not utilized in the following calculations.

The boundary conditions for the problem are specified for the potential ϕ and the current densities i_{\pm} . Since the intrinsic ζ potential is neglected, the boundary conditions of the potential is given by the external applied voltage,

$$\phi(x,t)|_{x=0} = V_0 e^{i\omega t},$$
(3.47a)

$$\phi(x,t)|_{x=L} = -V_0 e^{i\omega t}.$$
 (3.47b)

At the walls the normal components of the current densities vanish, which for this situation results in the boundary conditions

$$i_+(x,t)|_{x=0} = 0,$$
 (3.48a)

$$i_+(x,t)|_{x=L} = 0,$$
 (3.48b)

$$i_{-}(x,t)|_{x=0} = 0,$$
 (3.48c)

$$i_{-}(x,t)|_{x=L} = 0.$$
 (3.48d)

The current densities are eliminated by inserting Eq. (3.46) into Eq. (3.45), resulting in the continuity equation

$$\partial_t \rho_{\pm} = D_{\pm} \nabla^2 \rho_{\pm} \pm \mu_{\pm} \nabla \cdot (\rho_{\pm} \nabla \phi). \tag{3.49}$$

To proceed analytically the continuity equation is linearized in the charge density. In the bulk electrolyte, i.e. halfway between the two charged plates located at x = 0 and x = L, the charge density is assumed to be $\rho_{\pm}(x,t)|_{x=L/2} = \rho_0$, leading to

$$\rho_{\pm}(x,t) = \rho_0 + \delta \rho_{\pm}(x,t), \qquad \delta \rho_{\pm}(x,t) |_{x=L/2} = 0.$$
(3.50)

The intrinsic ζ potential is assumed to be zero, thus a non-zero $\delta \rho_{\pm}$ is a result of the applied potential at the walls. In the Debye–Hückel limit, where the thermal voltage is supposed to be larger than the external applied voltage, $|\delta \rho_{\pm}| \ll \rho_0$ is obtained. Therefore, $\rho_{\pm} \nabla \phi$ can be substituted by $\rho_0 \nabla \phi$, which gives

$$\partial_t \delta \rho_{\pm} = D_{\pm} \nabla^2 \delta \rho_{\pm} \pm \mu_{\pm} \rho_0 \nabla^2 \phi. \tag{3.51}$$

Utilizing the Poisson equation to replace the potential with the charge densities, results in two coupled differential equations for $\delta \rho_{\pm}(x,t)$. In the following, the notation $f(x,t) \equiv \delta \rho_{+}(x,t)$ and $g(x,t) \equiv \delta \rho_{-}(x,t)$ has been adopted, and the resulting one dimensional coupled differential equations become:

$$\partial_t f = D_+ f'' - \frac{\mu_+ \rho_0}{\epsilon} (f - g), \qquad (3.52a)$$

$$\partial_t g = D_- g'' + \frac{\mu_- \rho_0}{\epsilon} (f - g). \tag{3.52b}$$

- Here the prime denotes the derivative with respect to x.

Time independent solution for an asymmetric electrolyte

As a first approach, the problem is solved for a time independent external applied potential at the walls, i.e. $\omega = 0$. The electrolyte is assumed to be asymmetric in both valence $Z_+ \neq Z_-$ and diffusivity $D_+ \neq D_-$, which implies that also the ionic mobilities are different $\mu_+ \neq \mu_-$. It is noted that the Einstein relation can be written as $D_{\pm} = (k_{\rm B}T/Z_{\pm}e)\mu_{\pm}$.

Since the problem is independent of time, the solutions of Eq. (3.52) are given as f(x,t) = f(x) and g(x,t) = g(x) resulting in zero left hand sides of the equations. Utilizing the Einstein relations, Eq. (3.52) can be rearranged to

$$f'' = \frac{\mu_{+}\rho_{0}}{D_{+}\epsilon} (f - g) = \frac{\rho_{0}e}{\epsilon k_{\rm B}T} Z_{+} (f - g), \qquad (3.53a)$$

$$g'' = -\frac{\mu_{+}\rho_{0}}{D_{-}\epsilon} (f - g) = -\frac{\rho_{0}e}{\epsilon k_{\rm B}T} Z_{-} (f - g).$$
(3.53b)

Forming the difference between Eq. (3.53a) and Eq. (3.53b) gives rise to a second order ordinary differential equation, with $\nu \equiv \rho_+ - \rho_- = \delta \rho_+ - \delta \rho_- = f - g$.

$$\nu'' = \frac{\rho_0 e}{\epsilon k_{\rm B} T} \left(Z_+ + Z_- \right) \nu = \frac{1}{\lambda_{\rm D,a}^2} \nu.$$
(3.54)

The solution of Eq. (3.54) is given by

$$\nu = \mathcal{C}_1 e^{x/\lambda_{\mathrm{D,a}}} + \mathcal{C}_2 e^{-x/\lambda_{\mathrm{D,a}}},\tag{3.55}$$

where C_1 and C_2 are integration constants to be determined from the boundary conditions.

The density difference ν between positive and negative charges is inserted into the Poisson equation obtaining an expression for the potential variation between the parallel plates. Integration yields

$$\phi = -\mathcal{C}_1 \frac{\lambda_{\mathrm{D,a}}^2}{\epsilon} e^{x/\lambda_{\mathrm{D,a}}} - \mathcal{C}_2 \frac{\lambda_{\mathrm{D,a}}^2}{\epsilon} e^{-x/\lambda_{\mathrm{D,a}}} + \mathcal{C}_3 x + \mathcal{C}_4.$$
(3.56)

In order to determine the integration constants from the known boundary conditions, Eqs. (3.47) and (3.48), expressions for the current densities are determined. f and g are found by combining Eqs. (3.55) and (3.53) and integrating.

$$f = \frac{Z_+}{Z_+ + Z_-} \left[C_1 e^{x/\lambda_{\rm D,a}} + C_2 e^{-x/\lambda_{\rm D,a}} \right] + C_5 x + C_6, \qquad (3.57a)$$

$$g = -\frac{Z_{-}}{Z_{+} + Z_{-}} \left[\mathcal{C}_{1} e^{x/\lambda_{\mathrm{D,a}}} + \mathcal{C}_{2} e^{-x/\lambda_{\mathrm{D,a}}} \right] + \mathcal{C}_{5}x + \mathcal{C}_{6}.$$
(3.57b)

The current densities are then found by insertion of Eqs. (3.56) and (3.57) into the Nernst–Planck equation (Eq. (3.46)).

$$i_{+} = -D_{+}\mathcal{C}_{5} - \mu_{+}\rho_{0}\mathcal{C}_{3},$$
 (3.58a)

$$i_{-} = -D_{-}C_{5} + \mu_{+}\rho_{0}C_{3}.$$
 (3.58b)

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Utilizing the boundary conditions of the current densities, Eq. (3.48), the constants are given as $C_3 = C_5 = 0$, which corresponds to zero current flow in the system in accordance with the time independent problem.

Another constraint of the system is necessary to determine the potential. The charge neutrality of the entire system can be expressed as an integral over ν ,

$$\int_{0}^{L} \nu \, \mathrm{d}x = 0. \tag{3.59}$$

Employing Eqs. (3.47) and (3.59) three equations for the integration constants C_1 , C_2 and C_3 are found. Solving the equations leads to the following constants,

$$C_4 = 0, \qquad C_1 = \frac{V_0 \epsilon}{\lambda_{D,a}^2} \frac{1}{(e^{L/\lambda_{D,a}} - 1)}, \qquad C_2 = -\frac{V_0 \epsilon}{\lambda_{D,a}^2} \frac{e^{L/\lambda_{D,a}}}{(e^{L/\lambda_{D,a}} - 1)}.$$
 (3.60)

Determination of the last constant C_6 is based on the character of $f = \delta \rho_+$ and $g = \delta \rho_-$. According to the definition, $\delta \rho_+$ and $\delta \rho_-$ are zero in the bulk electrolyte corresponding to x = L/2. Insertion of C_1 and C_2 in Eq. (3.57) and requiring f = 0 and g = 0 for x = L/2 results in $C_6 = 0$.

The final expressions for ϕ , $\delta \rho_+$, $\delta \rho_-$ and $(\rho_+ - \rho_-)$ are thus,

$$\phi(x) = -\frac{V_0}{(e^{L/\lambda_{\rm D,a}} - 1)} \left[e^{x/\lambda_{\rm D,a}} - e^{(L-x)/\lambda_{\rm D,a}} \right], \tag{3.61}$$

$$\delta\rho_{+}(x) = \frac{\rho_{0} e Z_{+}}{k_{\rm B} T} \frac{V_{0}}{(e^{L/\lambda_{\rm D,a}} - 1)} \left[e^{x/\lambda_{\rm D,a}} - e^{(L-x)/\lambda_{\rm D,a}} \right], \tag{3.62}$$

$$\delta\rho_{-}(x) = -\frac{\rho_0 \, e \, Z_{-}}{k_{\rm B} T} \frac{V_0}{(e^{L/\lambda_{\rm D,a}} - 1)} \left[e^{x/\lambda_{\rm D,a}} - e^{(L-x)/\lambda_{\rm D,a}} \right],\tag{3.63}$$

$$\rho_{+}(x) - \rho_{-}(x) = \frac{\epsilon}{\lambda_{\rm D,a}^{2}} \frac{V_{0}}{(e^{L/\lambda_{\rm D,a}} - 1)} \left[e^{x/\lambda_{\rm D,a}} - e^{(L-x)/\lambda_{\rm D,a}} \right].$$
 (3.64)

It is noted that the deviations in the charge distributions relate as

$$\delta\rho_{+}(x) = -\frac{Z_{+}}{Z_{-}} \,\delta\rho_{-}(x). \tag{3.65}$$

Thus, it is apparent that ions with the largest valence screens a larger part of the wall potential relative to the ions with smaller valence. That is, the system may screen the wall potential by moving less ions when they carry more charge.

In Fig. 3.10a the potential $\phi(x)$ scaled with the thermal voltage $k_{\rm B}T/e$ is shown as a function of distance x between the parallel plates scaled with the Debye length $\lambda_{\rm D,a}$. The utilized parameters are listed in Table 3.1, from which it is apparent that the valences are chosen as $Z_+/Z_- = 2$, and the distance between the plates is chosen rather small in order to emphasize the fields near the walls. The plot of the potential shows, how the wall potential is screened completely at a distance of ~ 5 $\lambda_{\rm D,a}$ from the walls. The deviation of positive $\delta \rho_+(x)$ and negative $\delta \rho_-(x)$ charge concentrations relative to the bulk charge concentration are plotted in Fig. 3.10b as a function of distance $x/\lambda_{\rm D,a}$ between the plates.



Figure 3.10: Solutions of the time independent problem. a) The potential scaled with the thermal voltage $\phi/(k_{\rm B}T/e)$, Eq. (3.61), as a function of distance between the plates scaled with the Debye length $x/\lambda_{\rm D,a}$. The wall potential is completely screened at a distance $\sim 5 \lambda_{\rm D,a}$ from the walls. b) Concentration deviations from the bulk charge density for positive ions of valence $Z_+ = 2$ and negative ions of valence $Z_+ = 1$. $\delta \rho_+$, Eq. (3.62), is plotted with a full line and $\delta \rho_-$, Eq. (3.63), is dashed.

Asymmetric Debye length	$\lambda_{\rm D,a} = 25\rm nm$
Permittivity	$\epsilon = 78\epsilon_0$
Distance between plates	$L = 30 \lambda_{\rm D,a}$
Wall potential amplitude	$V_0 = 10 \mathrm{mV}$
Thermal voltage	$k_{\rm B}T/e = 25{\rm mV}$
Positive ion valence	$Z_{+} = 2$
Negative ion valence	$Z_{-} = 1$

Table 3.1: Values used for plots of the analytical time independent solution.

Time dependent solution for a symmetric electrolyte

The next step before solving the full asymmetric time dependent problem, has been to calculate the potential and charge distributions in the time dependent but symmetric case. The diffusion constants, ionic mobilities and valences are thus supposed to be equal for the two types of ions, i.e. $D_+ = D_- = D$, $\mu_+ = \mu_- = \mu$ and $Z_+ = Z_- = Z$.

The solutions of Eq. (3.52) are assumed to have a time dependence corresponding to the time variation of the external applied voltage, and may be written $f(x,t) = f(x)e^{i\omega t}$ and $g(x,t) = g(x)e^{i\omega t}$. Inserting these expressions into Eq. (3.52) and dividing with $e^{i\omega t}$ results in the following coupled differential equations:

$$i\omega f = Df'' - \frac{\mu\rho_0}{\epsilon} (f - g), \qquad (3.66a)$$

$$i\omega g = Dg'' + \frac{\mu\rho_0}{\epsilon} (f - g).$$
(3.66b)

Combining Eqs. (3.66a) and (3.66b), and utilizing the Einstein relation, $D = (k_{\rm B}T/Ze)\mu$, results in the following fourth order ordinary differential equation for f;

$$-\lambda_{\rm D}^2 D f'''' + \left(D + i\omega \, 2\lambda_{\rm D}^2\right) f'' + \left(\omega^2 \, \frac{\lambda_{\rm D}^2}{D} - i\omega\right) f = 0. \tag{3.67}$$

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The solution of Eq. (3.67) is given by

$$f = \mathcal{C}_1 e^{\kappa_\alpha x} + \mathcal{C}_2 e^{-\kappa_\alpha x} + \mathcal{C}_3 e^{\kappa_\beta x} + \mathcal{C}_4 e^{-\kappa_\beta x}, \qquad (3.68)$$

where the constants in the exponents are

$$\kappa_{\alpha} = \sqrt{i\omega/D},\tag{3.69a}$$

$$\kappa_{\beta} = \sqrt{1/\lambda_{\rm D}^2 + i\omega/D}.$$
(3.69b)

g is found by insertion of Eq. (3.68) into Eq. (3.66a) and can be written

$$g = \left(\mathcal{C}_1 e^{\kappa_{\alpha} x} + \mathcal{C}_2 e^{-\kappa_{\alpha} x}\right) - \left(\mathcal{C}_3 e^{\kappa_{\beta} x} + \mathcal{C}_4 e^{-\kappa_{\beta} x}\right).$$

Forming the difference of Eqs. (3.68) and (3.70) yields an expression for the charge density difference $\rho_+ - \rho_- = f - g$:

$$f - g = 2 \left(\mathcal{C}_3 e^{\kappa_\beta x} + \mathcal{C}_4 e^{-\kappa_\beta x} \right).$$
(3.70)

The difference between positive and negative charge density can be introduced into the Poisson equation (Eq. (3.44)), which by integration leads to the potential,

$$\phi = -\frac{2}{\kappa_{\beta}^{2}\epsilon} \left(\mathcal{C}_{3} e^{\kappa_{\beta}x} + \mathcal{C}_{4} e^{-\kappa_{\beta}x} \right) + \mathcal{C}_{5}x + \mathcal{C}_{6}.$$
(3.71)

Utilizing Eq. (3.46), the current densities are found by insertion of Eq. (3.68) or Eq. (3.70) together with Eq. (3.71).

$$i_{+} = i\omega \frac{1}{\kappa_{\alpha}} \left(\mathcal{C}_{2} e^{-\kappa_{\alpha} x} - \mathcal{C}_{1} e^{\kappa_{\alpha} x} \right) + i\omega \frac{1}{\kappa_{\beta}} \left(\mathcal{C}_{4} e^{-\kappa_{\beta} x} - \mathcal{C}_{3} e^{\kappa_{\beta} x} \right) - \mu \rho_{0} \mathcal{C}_{5}, \qquad (3.72a)$$

$$i_{-} = i\omega \frac{1}{\kappa_{\alpha}} \left(\mathcal{C}_{1} e^{\kappa_{\alpha} x} - \mathcal{C}_{2} e^{-\kappa_{\alpha} x} \right) + i\omega \frac{1}{\kappa_{\beta}} \left(\mathcal{C}_{3} e^{\kappa_{\beta} x} - \mathcal{C}_{4} e^{-\kappa_{\beta} x} \right) + \mu \rho_{0} \mathcal{C}_{5}, \qquad (3.72b)$$

Applying the boundary conditions, Eqs. (3.47) and (3.48), results in six equations determining the integration constants, which are then given as:

$$\mathcal{C}_{1} = 0, \qquad \mathcal{C}_{3} = DV_{0} \epsilon \kappa_{\beta}^{2} / \mathcal{N}, \qquad \mathcal{C}_{5} = i 2 (1 + e^{\kappa_{\beta}L}) \kappa_{\beta} V_{0} \lambda_{D}^{2} \omega / \mathcal{N}, \\
\mathcal{C}_{2} = 0, \qquad \mathcal{C}_{4} = -e^{\kappa_{\beta}L} DV_{0} \epsilon \kappa_{\beta}^{2} / \mathcal{N}, \qquad \mathcal{C}_{6} = -i L (1 + e^{\kappa_{\beta}L}) \kappa_{\beta} V_{0} \lambda_{D}^{2} \omega / \mathcal{N}, \quad (3.73)$$

where $\mathcal{N} = 2D(e^{\kappa_{\beta}L} - 1) + i(e^{\kappa_{\beta}L} + 1)\kappa_{\beta}L\lambda_{\mathrm{D}}^{2}\omega.$

The final expressions for ϕ , $\delta \rho_+$, $\delta \rho_-$ and $(\rho_+ - \rho_-)$ are thus,

$$\phi(x) = -\frac{2}{\kappa_{\beta}^{2}\epsilon} \frac{DV_{0} \epsilon \kappa_{\beta}^{2}}{\mathcal{N}} \left[e^{\kappa_{\beta}x} - e^{\kappa_{\beta}(L-x)} \right] + \frac{i(1+e^{\kappa_{\beta}L})\kappa_{\beta}V_{0}\lambda_{D}^{2}\omega}{\mathcal{N}} \left[2x - L \right], \quad (3.74)$$

$$\delta\rho_{+}(x) = \frac{DV_{0} \epsilon \kappa_{\beta}^{2}}{\mathcal{N}} \left[e^{\kappa_{\beta} x} - e^{\kappa_{\beta} (L-x)} \right], \qquad (3.75)$$

$$\delta\rho_{-}(x) = -\frac{DV_{0}\epsilon\kappa_{\beta}^{2}}{\mathcal{N}}\left[e^{\kappa_{\beta}x} - e^{\kappa_{\beta}(L-x)}\right],\tag{3.76}$$

$$(\rho_{+} - \rho_{-})(x) = 2 \frac{DV_0 \epsilon \kappa_{\beta}^2}{\mathcal{N}} \left[e^{\kappa_{\beta} x} - e^{\kappa_{\beta}(L-x)} \right].$$
(3.77)

Debye length	$\lambda_{\rm D} = 30{\rm nm}$
Permittivity	$\epsilon = 78\epsilon_0$
Distance between plates	$L = 30 \lambda_{\rm D}$
Wall potential amplitude	$V_0 = 10 \mathrm{mV}$
Diffusivity	$D = 2 \times 10^{-9} \mathrm{m^2/s}$
Debye frequency	$\omega_D = 2.2 \mathrm{MHz}$

Table 3.2: Values used for plots of the time dependent analytical solution for symmetric ions.

In Appendix A the Mathematica program employed for solving and plotting the equations is given. Values used for the plots are listed in Table 3.2, and in Fig. 3.11, Figs. 3.12 and 3.13 plots of the potential ϕ and charge density deviations, $\delta \rho_+$ and $\delta \rho_-$, are shown. The potential is scaled by the thermal voltage $k_{\rm B}T/e$ and the plate distance with the Debye length $\lambda_{\rm D}$.



Figure 3.11: Solutions of the time dependent problem at 1 kHz. a) The potential scaled by the thermal voltage $\phi/(k_{\rm B}T/e)$, Eq. (3.74), as a function of distance between the plates $x/\lambda_{\rm D}$. b) Negative charge density deviation $\delta\rho_{-}$, Eq. (3.76), is plotted with a full line and $\delta\rho_{+}$, Eq. (3.75), is dashed. For this low frequency, the solution corresponds to the time independent case.



Figure 3.12: Solutions of the time dependent problem at 100 kHz. a) The potential scaled by the thermal voltage $\phi/(k_{\rm B}T/e)$, Eq. (3.74), as a function of distance between the plates $x/\lambda_{\rm D}$. b) Negative charge density deviation $\delta\rho_-$, Eq. (3.76), is plotted with a full line and $\delta\rho_+$, Eq. (3.75), is dashed. The screening is no longer complete and the charge density deviation has decreased relative to the time independent case.



Figure 3.13: Solutions of the time dependent problem at 2.2 MHz. a) The potential scaled by the thermal voltage $\phi/(k_{\rm B}T/e)$, Eq. (3.74), as a function of distance between the plates $x/\lambda_{\rm D}$. b) Negative charge density deviation $\delta\rho_-$, Eq. (3.76), is plotted with a full line and $\delta\rho_+$, Eq. (3.75), is dashed. At this Debye frequency of the system, the screening is absent and oscillations occurs in the charge density deviation.

The low frequency solution, plotted in Fig. 3.11 for 1 kHz, corresponds to the time independent symmetric case. For a frequency of 100 kHz the screening of the wall potential is no longer complete, as seen from Fig. 3.12a, and the charge density deviations starts to decrease. At the Debye frequency of the system $\omega_D = D/\lambda_D^2$, the ions are no longer able to follow the shifting wall potential and the screening is absent, as seen from the plotted potential in Fig. 3.13a. The corresponding charge density deviations have in this frequency regime oscillations near the wall, Fig. 3.13b. The length scale of the oscillations decrease when the frequency is further increased. The wall potential frequency, for which these oscillations start to occur, depends on the distance L between the walls. When the distance increases, the frequency decreases, i.e., the oscillations start at lower wall potential frequency for increased L. For $\omega \to \infty$ the length scale of the oscillations becomes 0 and the oscillations vanishes. That is, when the oscillations begin, the ions does not screen the wall potential efficiently any longer, and for very high frequencies the oscillations stops and ion motion is completely absent.

Time dependent solution for an asymmetric electrolyte

Finally the asymmetric, time dependent problem is attended. The ionic diffusion constants are allowed to differ $D_+ \neq D_-$, implying that also the ionic mobilities are unequal $\mu_+ \neq \mu_-$. The ionic valances are, though, assumed to be equal $Z_+ = Z_- = Z$, in order to keep the problem simple. Solution of the equations is completed in accordance with the calculations performed for the symmetric electrolyte.

The solutions of Eq. (3.52) are expected to have the forms $f(x,t) = f(x)e^{i\omega t}$ and $g(x,t) = g(x)e^{i\omega t}$. By insertion in Eq. (3.52), the following coupled differential equations appear:

$$i\omega f = D_+ f'' - \frac{\mu_+ \rho_0}{\epsilon} (f - g), \qquad (3.78a)$$

$$i\omega g = D_{-}g'' + \frac{\mu_{-}\rho_{0}}{\epsilon} (f - g).$$
(3.78b)

The above equations are combined, and employing the Einstein relation $D_{\pm} = (k_{\rm B}T/Ze)\mu_{\pm}$, the resulting fourth order ordinary differential equation becomes

$$-2\lambda_{\rm D}^2 f'''' + \left[2 + i\omega \, 2\lambda_{\rm D}^2 \left(\frac{1}{D_-} + \frac{1}{D_+}\right)\right] f'' + \left[\omega^2 \, \frac{2\lambda_{\rm D}^2}{D_+ D_-} - i\omega \left(\frac{1}{D_-} + \frac{1}{D_+}\right)\right] f = 0.$$
(3.79)

The solution of Eq. (3.79) may be written

$$f = \mathcal{C}_1 e^{\kappa_{\alpha} x} + \mathcal{C}_2 e^{-\kappa_{\alpha} x} + \mathcal{C}_3 e^{\kappa_{\beta} x} + \mathcal{C}_4 e^{-\kappa_{\beta} x}, \qquad (3.80)$$

where the constants in the exponents are more complicated than in the symmetric case.

$$\kappa_{\alpha} = \sqrt{\frac{1}{2\lambda_{\rm D}^2} + \frac{i\omega}{2} \left(\frac{1}{D_-} + \frac{1}{D_+}\right) - \frac{1}{2}\sqrt{\frac{1}{\lambda_{\rm D}^4} - \omega^2 \left(\frac{1}{D_-} - \frac{1}{D_+}\right)^2},\tag{3.81a}$$

$$\kappa_{\beta} = \sqrt{\frac{1}{2\lambda_{\rm D}^2} + \frac{i\omega}{2} \left(\frac{1}{D_-} + \frac{1}{D_+}\right) + \frac{1}{2}\sqrt{\frac{1}{\lambda_{\rm D}^4} - \omega^2 \left(\frac{1}{D_-} - \frac{1}{D_+}\right)^2}.$$
 (3.81b)

Inserting Eq. (3.80) into Eq. (3.78a) yields

$$g = \left[i\omega\lambda_{\rm D}^2 \left(\frac{1}{D_+} - \frac{1}{D_-} \right) + \lambda_{\rm D}^2 \sqrt{\frac{1}{\lambda_{\rm D}^4} - \omega^2 \left(\frac{1}{D_-} - \frac{1}{D_+} \right)^2} \right] \left(\mathcal{C}_1 e^{\kappa_{\alpha} x} + \mathcal{C}_2 e^{-\kappa_{\alpha} x} \right) \\ + \left[i\omega\lambda_{\rm D}^2 \left(\frac{1}{D_+} - \frac{1}{D_-} \right) - \lambda_{\rm D}^2 \sqrt{\frac{1}{\lambda_{\rm D}^4} - \omega^2 \left(\frac{1}{D_-} - \frac{1}{D_+} \right)^2} \right] \left(\mathcal{C}_3 e^{\kappa_{\beta} x} + \mathcal{C}_4 e^{-\kappa_{\beta} x} \right)$$
(3.82)

From Poisson's equation, Eq. (3.44), the potential can be found as

$$\phi = \frac{2\lambda_{\rm D}^2}{\epsilon} \left[i\omega \frac{1}{D_+\kappa_{\alpha}^2} - 1 \right] \left(\mathcal{C}_1 e^{\kappa_{\alpha}x} + \mathcal{C}_2 e^{-\kappa_{\alpha}x} \right) + \frac{2\lambda_{\rm D}^2}{\epsilon} \left[i\omega \frac{1}{D_+\kappa_{\beta}^2} - 1 \right] \left(\mathcal{C}_3 e^{\kappa_{\beta}x} + \mathcal{C}_4 e^{-\kappa_{\beta}x} \right) + \mathcal{C}_5 x + \mathcal{C}_6 \left(\frac{1}{2} + \frac$$

Eq. (3.46) leads to the current densities, given by

$$i_{+} = i\omega \frac{1}{\kappa_{\alpha}} \left(\mathcal{C}_{2} e^{-\kappa_{\alpha} x} - \mathcal{C}_{1} e^{\kappa_{\alpha} x} \right) + i\omega \frac{1}{\kappa_{\beta}} \left(\mathcal{C}_{4} e^{-\kappa_{\beta} x} - \mathcal{C}_{3} e^{\kappa_{\beta} x} \right) - \mu_{+} \rho_{0} \mathcal{C}_{5}, \qquad (3.84a)$$

$$i_{-} = \mathcal{G}_{\alpha} \left(\mathcal{C}_{1} e^{\kappa_{\alpha} x} - \mathcal{C}_{2} e^{-\kappa_{\alpha} x} \right) + \mathcal{G}_{\beta} \left(\mathcal{C}_{3} e^{\kappa_{\beta} x} - \mathcal{C}_{4} e^{-\kappa_{\beta} x} \right) + \mu_{-} \rho_{0} \mathcal{C}_{5}.$$
(3.84b)

Above,

$$\mathcal{G}_{\alpha} \equiv \kappa_{\alpha} \left[i \omega \frac{D_{-}}{D_{+}} \left(\frac{1}{\kappa_{\alpha}^{2}} - 2\lambda_{\mathrm{D}}^{2} \right) + 2D_{-} \left(\lambda_{\mathrm{D}}^{2} \kappa_{\alpha}^{2} - 1 \right) \right], \qquad (3.85a)$$

$$\mathcal{G}_{\beta} \equiv \kappa_{\beta} \left[i\omega \frac{D_{-}}{D_{+}} \left(\frac{1}{\kappa_{\beta}^{2}} - 2\lambda_{\mathrm{D}}^{2} \right) + 2D_{-} \left(\lambda_{\mathrm{D}}^{2} \kappa_{\beta}^{2} - 1 \right) \right].$$
(3.85b)

Debye length	$\lambda_{\rm D} = 30{\rm nm}$
Permittivity	$\epsilon = 78\epsilon_0$
Distance between plates	$L = 30 \lambda_{\rm D}$
Wall potential amplitude	$V_0 = 10 \mathrm{mV}$
Diffusivity of negative ions	$D_{-} = 10^{-11} \mathrm{m}^2/\mathrm{s}$
Diffusivity of positive ions	$D_+ = 2 \times 10^{-9} \mathrm{m}^2/\mathrm{s}$
Debye frequency of neg. ions	$\omega_{D_{-}} = 11 \mathrm{kHz}$
Debye frequency of pos. ions	$\omega_{D_+} = 2.2 \mathrm{MHz}$

Table 3.3: Values used for plots of the time dependent analytical solution for asymmetric ions.



Figure 3.14: Solutions of the asymmetric time dependent problem at 1 kHz. a) The potential scaled by the thermal voltage $\phi/(k_{\rm B}T/e)$ as a function of distance between the plates $x/\lambda_{\rm D}$. b) Negative charge density deviation $\delta\rho_{-}$ is plotted with a full line and the positive charge density deviation $\delta\rho_{+}$ is dashed. For this frequency the fast positive ions are screening the slow negative ions, which are delayed relative to the changing potential.

The boundary conditions Eqs. (3.47) and (3.48) are applied, and the resulting equations are solved to determine the six unknown integration constants. A Mathematica program for calculation and insertion of these constants into the expressions for potential and charge densities is shown in Appendix A. In Figs. 3.14 and 3.15 the potential ϕ and charge distributions $\delta \rho_{-}$ and $\delta \rho_{+}$ are plotted using the values listed in Table 3.3.

In Fig. 3.14 the solution is plotted for 1 kHz. The potential distribution in Fig. 3.14a shows an incomplete screening of the wall potential. From Fig. 3.14b it is seen how oscillations in the negative charge density deviation $\delta \rho_{-}$ are present due to the low diffusivity, which implies that the ions are unable to follow the changing potential. Consequently, the much faster positive ions both screen these oscillations and a large part of the wall potential. When the frequency ω increases, the amplitude and length scale of the oscillations in $\delta \rho_{-}$ decreases, resulting in a more complete screening of the wall potential. Well above the Debye frequency for the slow negative ions $\omega_{D_{-}}$, the screening again becomes incomplete. When the frequency is increased, the screening of the wall potential decreases and oscillations in the positive charge density deviation $\delta \rho_{+}$ appears. In accordance with the symmetric case, the wall potential frequency, for which the oscillations begins, depends on the distance L between the plates. At the Debye frequency for the faster ions $\omega_{D_{+}}$ the screening is absent corresponding to a potential distribution as shown in Fig. 3.13a.



Figure 3.15: Charge density deviations of the time dependent problem at 2.2 MHz. a) The charge density deviation $\delta \rho_+$ for the positive ions. b) Charge density deviation $\delta \rho_-$ for negative ions. The screening is absent for this frequency, and oscillations appear for both negative and positive charge density deviations.

For this frequency ω_{D_+} the charge density deviations are shown in Fig. 3.15. The length scale of the oscillations in the negative charge density deviation is short compared to the positive charge density deviation, for which the diffusivity is larger. Furthermore, the absolute value of $\delta \rho_-$ is small compared to $\delta \rho_+$, reflecting that the motion of the slow negative ions stops at a lower frequency compared to the faster positive ions.

3.4 Summary

A one dimensional model of a two electrode system has been analyzed analytically, in order to see which effect asymmetric electrolytes have on the potential and charge distribution when alternating voltage is applied to the electrodes.

The problem was first solved independently of time, where it was concluded that a Debye length dependent on the valences of the idividual ions should be introduced. Moreover, it was seen that the ions shield the wall potential asymmetrically and that the ions of largest valence shield a larger part of the wall potential.

For the time dependent case solved subsequently, the solutions of the fully symmetric problem showed two characteristic frequencies of the system. One was the Debye frequency at which the ions no longer are able to screen the wall potential, whereby the potential distribution between the plates become a straight line. At very low frequencies, the ions screen the wall potential completely and the system approaches the time independent situation. For intermediate frequencies, the wall potential is partly screened, and another characteristic frequency exists, for which oscillations in the charge distribution occur. The specific value of this frequency was seen to depend on the distance between the parallel plates. The length scale of the oscillations decreases for increased frequency.

In the case of an asymmetric electrolyte the same two characteristic frequencies are present and they differ for the two ions. For a range of low frequencies, the wall potential screening is decreased because of the slow ions, and at higher frequencies (above the smallest Debye frequency) the screening is nearly equal to the symmetric case.

Chapter 4

System design

In the present chapter, considerations and decisions behind dimensions and geometries of the final fabricated micropumps are presented.

A schematic drawing of the final chip is presented in Fig. 4.1 to give an overview of the different elements that was considered during the design phase. The chip is comprised of transparent pyrex glass wafers, with metal electrodes defined at the bottom and channels with inlet holes contained in the top wafer. For illustration purposes the two chip layers have been separated. In the final system the two wafers are carefully aligned and subsequently bonded together.



Figure 4.1: An overview of the fabricated chip consisting of two glass wafers bonded together. In the top wafer the channel is etched and inlet holes for the liquid are made. Flow-generating electrodes are defined at the bottom wafer.

4.1 AC electrode micropump

Several factors had an impact on the final chip design. Not only the electrode array generating the liquid flow had to be considered, but also more practical issues such as chip materials and detection methods.

As a first approach it should be possible to reproduce some of the results obtained earlier by other groups, and it was decided to take the electrode geometry of Studer *et al.* [3] as a starting point in the design of the microfabricated pumps. The chip should be fabricated using the available cleanroom facilities of DANCHIP, which introduces limitations on the choice of materials and dimensions of both electrodes and channels. To facilitate determination of the pumping velocity, certain requirements regarding the channel design and the chosen type of substrate had to be fulfilled. Combined with rough estimates of typical parameter values within the system, a final design of electrodes and channels was composed as shown in Fig. 4.2.

Figure 4.2: The design of a single chip as it has been fabricated. It is marked A100 referring to the electrode periodicity of 100 μ m. The red areas are etched into the upper wafer and becomes channels or spacing above the contact pads. The black contours are metal defining the electrodes on the bottom wafer. The insert shows an enlargement of the designed electrode array. In each of the channel ends the positions of the inand outlet holes are marked.

4.1.1 Channels

First of all, it was decided to use a transparent material as substrate, since it allows for an easy optical detection of the flow velocity. The intension was to use different methods of detection, dependent on the parameters that should be investigated, and it seemed as the best solution to use glass wafers for both top and bottom layer. It would then be possible

4.1. AC ELECTRODE MICROPUMP

to view the channels from above using a light transmission microscope. Furthermore, it was intended to use Micro Particle Image Velocimetry (μ -PIV), and in this connection bead detection through the bottom wafer would be advantageous, since the external tubing limits the accessibility from above. An additional option would be to use optical tweezers to fix a particle at a certain position in the channel, thereby being able to measure the force, and hence the liquid velocity at that exact location, during steady fluid flow.

The above mentioned detection methods require that small beads are inserted into the channel and distributed in the liquid to facilitate a velocity measurement. Given that the dielectric constant¹ of the available beads differs from that of the electrolyte, dielectrophoretic effects would be of importance if the beads entered the channel area covered with electrodes. Furthermore, it is not known how the flow-pattern above the electrodes would be affected by the possible occurrence of beads in the vicinity of the metal surface. Consequently, the channel was designed as indicated in Fig. 4.3 with approximately half of the channel area covered with electrodes (marked by bars), and an area without electrodes between two inlet holes dedicated to velocity measurements (marked by dots). With the purpose of avoiding external pressure differences, the channel ends are connected in a closed loop by the outer tubing during the velocity measurements. As preparation, the beads can be inserted into the measurement area through the narrow side channel while letting electrolyte out of the channel end. This is explained in further detail in Section 6.2.

Figure 4.3: A schematic drawing of the channel design. To avoid beads in the channel area covered with electrodes, the small upper side channel is added as a bead inlet. During the flow measurements this side channel and the electrolyte outlet are sealed off, and the electrolyte is guided in a closed outer pump loop avoiding external pressure differences. The detection area filled with beads is indicated with dots, and the electrode area is marked with vertical bars.

The outer tubes are connected to the inlet holes through a sample holder clamped around the chip, as explained in Section 6.1, which requires a certain spacing of the inlet holes. In addition, optical velocity determination is not possible in the vicinity of the interface between the inlets and the outer tubes. Thus, the channel has been designed to

¹The dielectric constant of polystyren is 2.0-2.8.

allow a sufficiently large distance between the inlets and clear the detection area of sample holder components.

To ensure optimal visibility and working space, the channels should preferably have been much longer. However, a long channel results in an increased hydraulic resistance and consequently a lower liquid velocity, as seen from Eq. (2.17) in Section 2.3. Since a low flow resistance is desirable in order to detect liquid motion in low-voltage regimes, there will be a trade-off between working space and flow resistance. Furthermore the wafer area covered by each chip should be minimized in order to increase the number of different chip designs that can be realized on a single wafer.

4.1.2 Electrodes

To investigate how the translation period of the electrode arrays influences the pumping speed, it was decided to produce pumps having three different electrode periods. Starting with the work of Studer *et al.* [3] an electrode array of period length 50 μ m was chosen and the electrode lengths and spacings were copied. Scaling this geometry by respectively one and a half and two, translation periods of 75 μ m and 100 μ m with electrode widths as outlined in Table 4.1 were produced. In Fig. 4.4 the notation of the geometry is defined. Each micropump was named according to the translation period of the electrode array and marked A (Asymmetric). The fourth geometry listed in the table is a test structure with a symmetric electrode array, which is marked S (Symmetric). The motivation for upscaling the geometry, though theory predicts a higher velocity for shorter translation periods,

Figure 4.4: To make a rough estimate of the pure ohmic resistance of the entire electrode array on a micro pump chip containing a dilute electrolyte, each of the electrode spacings are approximated by resistors. Gaps of alternating sizes gives rise to two different resistor values approximated by the resistance of the liquid cube filling out the entire channel space between the electrodes, these cubes are indicated by dotted lines. The array of resistors is parallel coupled.

	Transl.	Pairs per	l_E	l_e	l_G	l_g	Η	h	W
	per. $[\mu \mathrm{m}]$	array, p	$[\mu m]$	$[\mu m]$	$[\mu m]$	$[\mu m]$	[µm]	$[\mu m]$	$[\mu m]$
A50	50	39	25.7	4.2	15.6	4.5	33.6	0.40	967
A75	75	26	38.5	6.3	23.4	6.8	33.6	0.40	967
A100	100	20	51.4	8.4	31.2	9.0	33.6	0.40	967
S75	75	26	22.5	22.5	15.0	15.0	33.6	0.40	967

Table 4.1: The chosen geometries in the four types of fabricated micro pumps. Since the length of the channel occupied with electrodes is the same for all pump types, the number of electrode pairs per array has to change. Every chip contains 8 arrays of electrodes.

Section 3.2, arose from problems experienced during fabrication of the first generation of induced charge micropumps [19]. The definition of the electrodes caused problems that could become worse if the electrode spacing was decreased. In Section 5.1 it is described how the electrodes are constructed on top of the glass wafer and apparently, this process was often unsuccessful resulting in a single short circuit between a pair of electrodes rendering the hole chip unusable. This is also the reason why the chip array in the present design is divided into eight identical arrays short circuited at the contact pad (see Fig. 4.2). The eight electrical wires leading to the active electrode arrays are very thin in the region adjacent to the contact pads, thereby making it easier to disconnect a malfunctioning array. Consequently, it would not be necessary to discard the whole chip. The electrodes have been numbered to simplify the process of locating and subsequently disconnecting a short circuited array section.

Based on an estimate of the total ohmic resistance of the electrode array in the channel containing a dilute solution of salt, an optimal cross sectional area of the electrical wires could be determined. As indicated in Fig. 4.4, the resistance of the fluid that can support a current between two adjacent electrodes was roughly estimated as the resistance of the liquid cube filling out the total channel volume between two electrodes. The resistance of such a cube is given by $R = l/(\sigma w H)$, where σ is the conductivity of the liquid. The length l of the cubes corresponds to the electrode gaps l_G and l_g . w and H are the channel width and height, respectively. The two different electrode gaps give rise to different resistances, R_G and R_g . If the electrode array consists of p electrode pairs and correspondingly p pairs of gaps, the array is approximated by 2p resistances of alternating size, all coupled in parallel. Furthermore, the whole chip consists of eight arrays coupled in parallel, resulting in a total pure ohmic resistance in the order of

$$R_{\rm chip} = \frac{1}{8p} \left(\frac{R_G R_g}{R_G + R_g} \right). \tag{4.1}$$

To ensure that the resistances of the electrical wires are negligible, the above estimate of the ohmic fluid resistance has been underestimated on purpose. There are several reasons why this estimate is too low. For instance, the current is in fact limited to a much smaller area as the electrodes only occupy a small fraction of the total cross sectional area.

It would be reasonable to make the electrical wires as wide and thick as possible in order to minimize the resistance, however, this is not possible due to limitations imposed

	Pt	Au	Al	Ti
Resistivity, $\rho [10^{-8} \Omega m]$	10.6	2.35	2.66	40.0

Table 4.2: Resistivity at 20°C for some metals considered as electrodes in the induced charge EO pump.

by the fabrication process. The bonding process, described in Section 5.1, requires a certain minimum distance between the electrode structures and is enhanced as the electrode thickness is decreased. As mentioned in connection with the channel design, it is also preferable to have a small chip, whereby the number of chips per wafer is increased.

Utilizing Eq. (4.1) for chip A50 filled with 0.1 mM KCl solution gives a resistance of 226 Ω . In comparison the electrical wire leading to the array farthest from the contact pad has a resistance of 21 Ω . This is the resistance, $R = \rho \times \text{length}/(\text{width} \times \text{height})$, for a platinum electrode of length 2 cm, height 400 nm and width 250 µm. The four pairs of electrical wires leading to the four arrays closest to the contact pads are half as wide as the four pairs farthest away from the contact pads, since they on average are correspondingly shorter, which results in the same resistance. If aluminum had been used as electrode material instead, the resistance of the electrical wires with the same dimensions had been in the order of 5 Ω , corresponding to the difference in resistivity of the metals, outlined in Table 4.2.

The choice of electrode material does not only depend on the resistivity of the metal, but also on the durability of the metal during pumping, where a low frequency AC current is applied while the electrodes are exposed to an electrolyte. Aluminum is a quite soft material, and as explained in Section 5.1, the Al surface additionally becomes distorted during fabrication, making the electrode thickness difficult to control for this metal. The group of Ramos *et al.* has reported problems with wearing of pure Au-electrodes. Titanium would be good choice regarding robustness, however, the resistivity of this metal is 15 times the resistivity of aluminum and gold. Consequently, this electrode material would introduce additional resistances in the electrical circuit. Platinum is another alternative being robust and having a relatively low resistivity. This was also the starting point in this fabrication process, since Pt was the metal used by Studer *et al.*

Finally, it should be noted that a number of ruler lines have been placed within and just beside the channel in the detection area as guidance during the velocity measurements. The lines are defined in the electrode material and the spacing is exactly 200 μ m. These can be seen in Fig. 4.2.

4.2 Test structures

A number of simpler channel and electrode structures were designed along with the micropump chips to gather information about the basic behavior of the system under investigation. It may be clear from Chapter 3 that the entire system of electrodes and electrolyte in the pump construction interacts in a rather complex way. Measurements on very simple electrode structures could thus increase the general understanding of the problem.

Figure 4.5: Test chips containing two electrode systems. The electrodes in a) are very wide in order to simplify the mathematical modelling of the system. The insert shows a magnification of the gap, which is $10 \,\mu\text{m}$ wide. The geometries in b) are copied from the work of Green *et al.* [5], and the magnified gap is $25 \,\mu\text{m}$.

In Fig. 4.5 two different chips containing two electrode systems are shown. These capacitors, characterized by having the conducting plates positioned beside each other instead of the usual two layer configuration, could correspond to one pair of electrodes in the induced charge EO micro pump. The very wide capacitor plates in Fig. 4.5a are chosen to make it as simple as possible to model the system. In this way, the system may be modelled as a gap between two half infinite metal plates interacting with an electrolyte. This is a valid approximation, since the electrical field affecting the ions is concentrated in the vicinity of the electrode spacing. In Fig. 4.5b the electrodes constituting the capacitor have the exact same geometry as seen in the work of Green et al. [5], and they were constructed in order to compare results obtained in the present project with former work.

The chip designs depicted in fig Fig. 4.6 are made with the purpose of controlling the material parameters of the fabricated pumping system. Fig. 4.6a shows a chip made for conductivity measurements of the electrolyte applied during pumping over the asymmetric electrode array. In Fig. 4.6b a test structure for electrode resistance measurements is illustrated.

4.3 Mask layout

Fig. 4.7 shows the final layout for the entire wafer. The design contains five chips in total that should be able to pump an electrolyte, as well as a number of test structures including two chips with symmetric electrode arrays. With the exception of the chip dedicated to conductivity measurements, the test chips have been placed where the unused wafer area

Figure 4.6: Test chips designed for four-point measurements of a) the electrode resistance and b) the conductivity of the electrolyte utilized to generate pumping above the electrode array.

is insufficient to contain an entire micropump.

To make the oxidation of the electrodes possible, all electrodes are connected to one of the big contact pads marked A and B, respectively. These connections are broken when the chips are diced. As mentioned in Section 3.2, it was considered wether to introduce alternating oxide thickness in the electrode array, and each of the two contact pads on a single chip were therefore connected to the A and B electrode, respectively. The oxide thickness may be controlled by the voltage level applied to the electrode during oxidation, and applying different voltages to the A and B electrodes would result in alternating thickness on the electrodes in the array.

The structures not mentioned in this chapter were made for fabrication control purposes.

Figure 4.7: The design of the entire wafer consisting of three different layers corresponding to three photolithography processes. The black layer 1 is the mask used for definition of the electrodes, and the red layer 4 is used to define the channel areas. Also the mask for definition of in- and outlet holes is shown as the gray layer 3.
Chapter 5

Fabrication

The induced charge EO micropump is constructed out of materials suitable for lab-ona-chip applications. At the beginning of the project no process flow existed, but it was decided to fabricate a channel containing electrodes at the bottom and inlet holes for liquid injection. Placing electrodes within a channel that should be perfectly sealed was a considerable challenge, and fluid leakage had already proved to be one of the biggest problems during fabrication of the first generation micropumps [19]. Many issues regarding the final process flow had to be taken into consideration prior to the fabrication phase, and the most important decisions made during this planning phase are explained in Section 5.2.

As shown in Fig. 4.1 it was decided to define the electrodes on one wafer and bond it together with another wafer containing channels and inlet holes. The fabrication of in- and outlet holes ended up causing a host of trouble and being extremely time consuming. If the holes were drilled after bonding of the two wafers, dust and glass pieces would inevitably be introduced into the channel, which could possibly disturb the flow or eventually hinder fluid flow completely. Consequently, it was decided to etch both the holes and the channels before bonding the two wafers. Unfortunately this etching procedure relied on old clean room equipment, that turned out to be very unstable and finally became inoperable due to permanent machine breakdown. In Section 5.3, the attempts and complications of etching in- and outlet holes are described along with the process flow of the combined etching procedure.

As an alternative to the etching procedure, the in- and outlet holes were drilled in the bonded wafers, a method that nevertheless turned out to be quite successful. In the following section, the process flow behind the functional micro pump chips is explained.

5.1 Process flow

Fabrication of the chips containing micropumps has been based on standard cleanroom processing. The chips may be fabricated within a week, assuming that no problems regarding cleanroom facilities arise. However, it should be noted that the chips cannot be fabricated in the DANCHIP cleanroom presently due to the above mentioned machine breakdown.



Figure 5.1: An overview of the fabricated chip, where the shaded area indicates the bonding of the two wafers. The dashed line marks the cross section used in the illustrations of the process flows at Figs. 5.2 and 5.10.

Figs. 5.1 and 5.2 shows a summary of the process flow applied in the micropump fabrication. In Appendix B a more detailed overview is given, and the corresponding step by step process flow for use in the MIC cleanroom has been enclosed. Additionally all machine specifications and procedures are listed there.

Substrates

Glass wafers were chosen as substrates for both top and bottom layers, resulting in an entirely transparent chip. It was decided to use pyrex wafers, since they consist of ion contaminated glass suitable for anodic bonding performed as the last cleanroom fabrication step. Unfortunately, the content of ions also requires a more careful treatment in the cleanroom to avoid contamination of machines and baths normally used to process pure silicon wafers. As a result, only dedicated solutions and less clean machines can be used during the processing, introducing restrictions on the fabrication possibilities.

The wafers have a thickness of $0.5 \text{ mm} \pm 0.05 \text{ mm}$ and are not particle-free at delivery, so a cleaning must be performed. In order to remove dust and particles, a mechanical cleaning was first carried out by lowering the wafers into a solution of water and Triton x-100 soap, and applying ultrasound for 10 min. Subsequently, all organic remnants were removed by 10 min chemical cleaning in a Piranha solution consisting of approximately 75% H₂SO₄ and 25% H₂O₂.

5.1.1 Electrode wafer

Photolithography

The electrodes are defined by standard positive photolithography. A thin layer of photodefinable polymer is spun onto the wafer and subsequently exposed with UV light through

5.1. PROCESS FLOW



Figure 5.2: Summary of the process flow behind the functioning induced charge EO micro pumps. In the left column the process of the top wafer containing channels is shown, and in the right column the processing of the electrodes at the bottom wafer is summarized. Underneath these separated wafer fabrication steps, the assembling of a chip is illustrated. The depicted cross section is shown from above at Fig. 5.1.

a mask of patterned chromium placed close to the surface. The exposed photoresist then becomes more soluble in the liquid developer, which leaves the unexposed areas unaffected, and the mask pattern has thus been transferred to the polymer. For this process, a positive photoresist has been used. If instead a negative resist had been applied, the unexposed areas would have been dissolved [13].

When the substrate is UV transparent, it is necessary to prevent the light from being transmitted through the photoresist into the substrate, resulting in uncontrolled reflection of light and unwanted additional exposure. To avoid this, a thin, 10 nm, layer of aluminum was deposited on the pyrex substrate using a Leybold E-beam evaporator. This layer also provides a better adhesion of the photoresist on the hydrophilic Pyrex substrate.

The photoresist, applied in this fabrication process is used for rather thin resist layers and may be used for both positive and negative photolithographic processes. By introduction of an extra baking step during the exposure phase, it is possible to convert the photoresist from a positive type to a negative. This resist is spun onto the aluminum layer just after the deposition, in a $1.5 \,\mu\text{m}$ thick layer. The wafer is prebaked on a hotplate for 2 min at 90°C to drive off the remaining solvent, applied in order to control the photoresist viscosity.

In this photolithographic process, the invertibility of the used photoresist is utilized, since a negative process is necessary for a lift off process, as explained below. To obtain the most accurate pattern transfer during exposure of the photoresist, the mask is brought into contact with the resist. This technique is known as hard contact exposure. The chromium mask layout is shown in Fig. 4.7 in Section 4.3 as the black pattern (layer number 1). The wafer is subsequently exposed for 3 s, followed by a 100 s reversal bake on a 120 °C hotplate. Finally, the resist is exposed for 30 s (flood exposure) before the development for 60 s in a NaOH solution. This solution dissolves the layer of aluminum in the electrode pattern as well. The patterned photoresist is shown in Fig. 5.3.



Figure 5.3: Micrographs of the patterned photoresist used to define the electrodes (the light areas correspond to resist). Figure a) shows a part of the electrode array with a translation period of 50 μ m. In b) the on-chip test structures are depicted for line spacings of respectively 1 μ m, 2 μ m and 3 μ m. Here, the resist is patterned successfully down to a 2 μ m spacing.

Metal deposition and lift-off

Upon the photoresist layer, defining the electrode network, the electrode metal was deposited. Because of the negative photolithography process, the resist walls have a negative slope, as indicated in Fig. 5.4. The fringing effect of light passing an edge of the mask results in exposure of the resist just under the mask in the vicinity of all mask edges. When the photoresist is subsequently dissolved and the metal around the electrode pattern is lifted off, there is no risk for the process to be obstructed by unwanted connections between metal on top of the resist and metal deposited at the wafer surface.

Different types of electrodes were fabricated, however, only platinum electrodes were used for the functional chips. Using the Alcatel E-beam evaporator a 10 nm Ti layer was deposited to ensure good adhesion between the glass substrate and the platinum, followed by a 500 nm Pt deposition. The deposition rate, though, was lower than stated by the

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Figure 5.4: The electrodes are defined by lift off, requiring a negative photolithographic process, where the exposed photoresist remains on the wafer surface after development. Due to the fringing effect of light passing the mask edges, the resist walls become negatively inclined.

Alcatel deposition controller, and the electrodes had to be measured after the processing to determine their exact height.

Following metal deposition, the wafers were lowered into a clean acetone bath to dissolve the photoresist, and ultra-sound was applied for 15 min to enhance the metal lift off. Note that the process is improved when the corners are rounded in the vicinity of the finest electrode structures, which are shown in Fig. 5.5. Finally, the Al leftovers are stripped in developer. This lasts for 1 min and 20 s, upon which the electrode wafer is completed. The lift off process is inspected at the vertical bars of increasing spacing, which are placed at each chip. Fig. 5.6 shows successful lift off down to 3 μ m spacing, which is lower than the designed minimum spacing of 4.5 μ m.

The wafers were checked for short circuits with a multimeter connected to the big electrode pads A and B on each side of the wafer. Short circuiting of the electrodes did



Figure 5.5: Micrographs of the completed Pt electrodes on the Pyrex substrate. The pictures are from the same wafer and show a part of the fabricated electrode arrays for each of the three translation periods at the same microscope enlargement. The electrode array in a) has a translation period of 50 μ m, in b) the translation period is 75 μ m and c) shows a translation period of 100 μ m.



Figure 5.6: Inspection of the lift off process shows well-defined metal lines down to $3 \mu m$ spacing. Figure a) depicts the on-chip test structures of respectively $2 \mu m$ and $3 \mu m$ spacings, while b) shows an enlargement of the $3 \mu m$ test structure, corresponding to the black frame in a).

not seem to be a general problem, since only one or no fabrication errors were detected per wafer. The electrode heights and surface roughness for Pt and Al electrodes were measured using a Dektak stylus profilometer. The heights of the electrodes are $400 \text{ nm} \pm 5 \text{ nm}$, i.e. approximately 80% of the displayed height. The surface roughness is quite different for the two metal types. The Al electrodes have an approximate roughness of 15 nm, whereas the Pt surface level variation is in the region of 1.5 nm. Thus, Al electrodes has a surface roughness 10 times that of Pt electrodes. This difference can be explained by the final fabrication step, where the Al electrodes are damaged in the developer and the Pt surface is left unaffected.

5.1.2 Channel wafer

Sputtering of amorphous silicon

At the beginning of the channel fabrication process, a thin layer of amorphous silicon is deposited on the pyrex substrate, which is cleaned as previously explained. The sputtered Si layer has a double function in the further processing. First it acts as a mask during the channel etching, and secondly it serves as a diffusion barrier during the anodic bonding.

To activate the surface before the Si deposition, the wafer is placed in a Plasma Asher for 1.5 min at maximum power (1000 W). This step is introduced in order to replace an RF argon sputtering, as explained in Section 5.2. Subsequently, a layer of 100 nm amorphous silicon is deposited using a Varian sputtering system. The resulting layer is semitransparent and slightly pink as expected from a rough estimate of reflected wavelengths based on the refractive index of Si.¹ Since this a-Si layer is etched away in accordance with the channel pattern, the final chip has transparent channels, though it remains semitransparent around the channels.

Etching of channels

To define an etch mask for the silicon layer, a negative photolithographic process was performed. The process was chosen negative in order to make the alignment process easier. In this case, the sputtered Si layer ensures good adhesion of the photoresist and prevents UV light from proceeding into the substrate, thus serving the same purpose as the Al layer did in the processing of the electrode wafer. If the wafer processing is not continued less than two hours after silicon deposition, it should be dipped shortly (15 s) into a bath containing a 5% HF solution to etch away the native oxide. The photolithographic process is akin to the process in which the electrodes were defined, except that another mask is used and the deposited photoresist layer is thicker. Mask number 4 containing the channel pattern can be seen in Fig. 4.7, where it is indicated how all areas corresponding to the channels, in order to prevent the wafers from bonding at the contact pads. The resist is spun onto the wafer in a layer of 2.2 μ m, which must be exposed for 4 s due to the

¹Assuming normal incidence at a 100 nm thick Si layer of refractive index $n_{\rm Si} = 3.4$, there will be constructive interference between directly reflected wavelets and wavelets reflected from the Si-SiO₂ interface for wavelengths around $\lambda = 2 \times 100 \text{ nm} \times 3.4 = 680 \text{ nm}$ [14].

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slightly increased thickness. The rest of the photolithographic process is exactly the same as outlined for the electrode fabrication.

The wafer is briefly inspected before proceeding with etching of the silicon layer defined by the channel pattern. The back side of the wafer and the wafer edges are covered with blue tape, which is a thick etch resistant plastic foil that protects the wafer against the strong glass etch used at a later stage. The solution used for etching amorphous silicon is $HNO_3:BHF:H_2O$ mixed in the ratio 500:25:500. The etching process consists of two steps where the silicon is first oxidized by the nitric acid and this oxide is then dissolved by the hydrofluoric acid. The reaction scheme of the entire etch process is [15]:

$$Si + HNO_3 + 6HF \rightarrow H_2SiF_6 + HNO_2 + H_2 + H_2O.$$
 (5.1)

Since gas is developed during etching, the surface target is pointed upwards and the solution is placed on a magnetic stirrer to ensure continuously flow of the etchant. In a fresh mixture the etch rate is $\sim 100 - 400 \text{ nm/min}$, and the thin amorphous silicon layer is removed after approximately 1 min.

The wafer is baked in a 120°C oven for 25 min to harden the resist and improve its etch resistance. It should be noted that the blue tape is not damaged by this treatment. The wafer is now mounted in a special holder (shown in Fig. 5.7) fixing the wafer in a horizontal position with the channel structures facing upwards, and lowered into a plastic container with 40% hydrofluoric acid, which etches the glass with a rate of approximately $3.4 \,\mu\text{m/min}$ dependent on the specific circumstances. The reaction scheme of the etch is [15]:

$$\operatorname{SiO}_2 + 6\operatorname{HF} \rightarrow \operatorname{H}_2 + \operatorname{SiF}_6 + 2\operatorname{H}_2\operatorname{O}.$$
 (5.2)

The container is placed on a magnetic stirrer, circulating under the wafer to prevent nonuniform etching. After 8 min and 45 s the channels should have reached a depth of $30 \,\mu\text{m}$. The wafer is subsequently stripped for blue tape and photoresist in an acetone bath.

With the Dektak stylus profilometer, the depth of the channels was measured to $33.6 \,\mu\text{m}$, which translates into an effective etch rate of $3.8 \,\mu\text{m/s}$. The surface roughness of the channels were measured to be $2 - 4 \,\text{nm}$. In Fig. 5.8, micrographs of the etched channels are shown. The shadow along the edge indicates how the isotropic character of the etch results in etching of the glass underneath the a-Si layer.



Figure 5.7: Setup for 40% HF etch of Pyrex wafer. The wafer is placed in a special holder with the surface target pointing upwards. The holder leaves space for a magnet stirrer underneath the wafer in order to ensure uniform etching of the structures on the wafer surface.



Figure 5.8: Micrographs of the HF etched channel. a) shows a channel turn with a shadow along the rim where the glass has been etched away under the a-Si layer. b) is a magnification of the channel edge corresponding to the area in the black frame in a).

5.1.3 Wafer bonding and subsequent processing

Anodic bonding

Anodic bonding between a pyrex glass surface and a silicon surface brought into contact, is obtained by applying an electric field over the interface while heating the substrates. The pyrex glass is contaminated with positively charged sodium ions, which are free to move through the glass substrate when this is heated up. If the two substrates are placed between electrode plates with a large voltage difference, the sodium ions will move towards the negative electrode. A concentration gradient will built up in the glass, and a negatively charged depletion layer is formed nearby the substrate interface. The entire potential drop will thus be across the depletion layer and the substrate interface. The strong E-field causes oxygen ions in the depletion layer to become mobile and move towards the positively charged Si layer where they react, causing a strong bonding of the substrates [17].

In the present fabrication process, a silicon layer deposited on one of the two pyrex substrates, serves as diffusion barrier against the sodium ions. Furthermore, it was necessary during the bonding to place a Si wafer between the pyrex substrate and the positively charged electrode, to prevent the glass wafer from bonding directly to the electrode. An unpolished silicon wafer with a very rough surface was chosen so that bonding would not occur.

Before bonding, the wafers should be completely clean in order to prevent small particles from creating voids between the layers. Consequently, the top wafer containing channels was rinsed in a Piranha solution, which removes any residues accumulated during the fabrication process, such as tape and resist particles. However, the electrode wafer could be damaged in the Piranha solution, thus it was only cleaned with compressed N_2 gas in order to remove dust particles that settled after the fabrication. Concluding the bonding process, the wafers were aligned and pressed against each other between two metal plates, over which the voltage difference was applied. The first wafer set was bonded at 350° C by applying a voltage difference of 1000 V for 10 min. After this bonding, more voids than expected were observed between the electrode structures. During bonding of

5.1. PROCESS FLOW



Figure 5.9: Micrographs of a fabricated chip with translation period $100 \,\mu\text{m}$. The insert to the right shows a magnification of the flow-generating electrode array in the channel to the left and the ruler lines for velocity detection in the channel on the right side.

the next wafer, the applied temperature was increased to 400° C to soften the glass more and make it fit better around the electrodes. The voltage difference for this bonding process was only 700 V, since current break through was observed at higher voltages. Even so, the result was not significantly improved.

Dicing wafers and drilling holes

After bonding of the two different wafers, the chips were separated using a dicing saw outside the cleanroom. The narrow lines, defined in the electrode layer, have been used as guidance for the dicing. These can be seen in the mask design in Fig. 4.7. In addition to the wafer dicing, where both of the wafers were cut through, also dicing lines only cutting through the top wafer were applied to remove the piece of glass covering the electrical contact pads on each chip. In Fig. 5.9 micrographs of a finished chip is shown.

As the last fabrication step, three in- and outlet holes were drilled in each chip using a cylindrical diamond drill with a diameter of 0.8 mm. The drilling was performed in deionized water, which ensured an efficient cooling and prevented much of the glass dust from ending up inside the channel.

5.2 Challenges and considerations

Before the final process flow and chip design were established, many deliberations were done and several choices were made. Unstable machines and unexpected outcomes of the processing also led to revisions of the fabrication procedure. In this section, the most important decisions are explained.

5.2.1 Considerations behind the final process-flow

The motivation for choosing Pyrex glass as a substrate is partly substantiated in Section 4.1. Based on the detection methods considered in this section, a solution employing two transparent wafers is justified. Furthermore, the insulating nature of glass makes it suitable for the chosen chip design, since the electrodes are bonded directly between the substrate layers and should not be short circuited. Pure quartz wafers are also electrically insulating, but they do not contain Na⁺ ions needed for the anodic bonding, as earlier mentioned. An alternative process flow was also considered, in which a pure silicon wafer could be used for the bottom substrate instead of the contaminated Pyrex glass. Electrodes would then be defined above the Si wafer followed by deposition of a thick layer of SiO₂ using plasma enhanced chemical vapor deposition. On top of the SiO₂, a layer of Si should be deposited. The channels could subsequently be etched into the SiO₂ using Reactive Ion Etching and finally, a Pyrex wafer should be anodically bonded on top of the Si layer, thereby sealing the channels. This solution was not chosen because of the reduced detection possibilities. Furthermore, the height of the channel would be limited to a maximum size of 10 µm, which is smaller than desired.

Different bonding methods were also considered, especially because of the numerous problems that arose during fabrication of the first generation of micropumps [19]. Anodic bonding was viewed as the best option, though it is not the perfect solution, since the electrodes introduce non-uniformities at the surface, as explained in Section 5.2.2. Another commonly used bonding method, where the wafers are exposed in a heated KOH solution before they are pressed together, is unfortunately unsuitable for a Pyrex wafer containing electrodes. Due to the different expansion coefficients of glass and metal, the wafer cannot be heated to more than approximately 400°C, and the KOH bonding method only works at approximately 550°C.

In the process flow outlined in Section 5.3, both the channels and holes were defined by photolithography. An alternative approach was to cover the surfaces with blue tape and afterwards use a CO_2 laser to define the etch mask for channels and holes in the film. This solution would however introduce some problems regarding alignment of the holes in the two identical protective layers made of blue tape, which must be placed on both sides of the wafer during the sandblasting process. This alignment ensures that the holes are generated properly, but as Pyrex glass is not IR transparent it would be rather difficult to obtain a precise alignment. Hence, it was decided to use photolithography, where wafer alignment is a simple process.

5.2. CHALLENGES AND CONSIDERATIONS

5.2.2 Anodic bonding over electrodes

Anodic bonding requires plane surfaces to ensure an optimal result, however, it is possible to bond across non-uniformities if they are below a certain size, depending on the substrates to be bonded, the temperature and the voltage. When bonding Pyrex wafers around metal electrodes, it is possible to achieve a good result with an elevated temperature, because of the softened glass that fits around the electrodes. The temperature should nonetheless be kept under 400° C due to the different thermal expansions coefficients. The voltage could also be increased but is limited by the eventual occurrence of a current break through, which seemed to happen at lower voltages when the temperature was increased.

The bonding results of the fabricated wafers were good and most of the chips were properly sealed after dicing. Yet, the distance required to bond the wafers between two adjacent electrode structures was greater than expected. Based on the experimental findings it may be concluded that the wafers bond at a distance of $\sim 150-200 \,\mu\text{m}$ from an electrode structure of height 400 nm. Consequently, in some cases the chips leaked where the electrodes were placed close to the edge.

Small gaps in the vicinity of the channel were not considered as a problem. The hydraulic resistance, given by Eq. (2.18), of these tiny "extra channels", would be around $(33 \,\mu\text{m}/0.4 \,\mu\text{m})^3 \sim 5 \times 10^5$ times more than the resistance of the main channel, i.e. they would not affect the flow significantly and may be neglected during the flow measurements.

5.2.3 Sputter deposition of amorphous silicon on pyrex substrates

During the fabrication period the Varian sputter deposition machine needed for deposition of amorphous silicon broke down. The normal procedure for a-Si deposition begins with an RF argon sputter cleaning of the surface, where minor surface contaminations are removed in order to ensure good adhesion between the a-Si layer and the Pyrex substrate. This specific function broke down and another solution had to be found to make the a-Si film adhere.

Initially, attempts were made to deposit a-Si without any previous treatment of the surface, but this resulted in poor adhesion during the subsequent HF etch test. The same conclusion was reached when the surface was treated with an RF sputter cleaning in an Alcatel sputter deposition machine, possibly because the effect applied to the plasma was only 200 W. Finally it was tested how one minute of plasma ashing at 1000 W affected the adhesion. The result was very good, and the a-Si adhered to the surface during the entire HF etch.

Unfortunately, also the a-Si sputter function broke down later in the fabrication phase. The Alcatel sputter deposition machine was then employed for the a-Si deposition, but the results were not good and in addition, a substantial amount of calibration work was associated with the start-up. Much later in the project period, an oxygen leak was detected in the chamber of the Alcatel sputter deposition machine, which could explain the unsuccessful results.

5.2.4 Etching of in- and outlet holes

It was the original plan to etch in- and outlet holes in the top wafer during cleanroom fabrication in order to avoid the introduction of drilling dust into the channel. The process flow for the chip with etched holes is presented in Section 5.3. Processing of the holes ended up being the most time consuming part of the entire chip fabrication process, mainly because of equipment breakdown during the calibration phase of the etching procedure.

A process recipe developed in 1998 by Denninger [20] was used as a starting point in the process flow for the etching of holes through an entire glass wafer. The recipe though, was modified to meet the requirements of the new process design and had to be calibrated accordingly. This is also mentioned in Section 5.3.

During the fabrication phase, alternatives to the hole etching were considered once the poor condition of the equipment became clear. One possibility could have been to sand blast the holes through the wafer. However, this did not seem to be feasible whether the holes were blasted before or after the channel processing. Sand blasting is a dirty process performed outside the cleanroom and requires complete sealing of the wafer surfaces, which are covered with photoresist and blue tape patterned in accordance with the wanted hole positions. If the channels were etched in the first process steps, it would be difficult to cover the channel containing side of the wafer with photoresist, especially if a channel height of $30 - 50 \,\mu\text{m}$ was desired. Conversely, it would also be problematic to blast the holes in the first process step, since a thin layer of photoresist cannot be spun onto a surface covered with holes in order to define the channels.

It was also considered to change the substrate of the top wafer and use silicon instead of Pyrex glass. This substrate do not contain ions and may consequently be processed in all available cleanroom equipment. This removes many of the fabrication restrictions, nevertheless, it also results in new process flows, which must be calibrated. Due to time limitations a new process flow was not realized.

5.3 Etching inlet holes

In this section, the originally planned process flow is presented and the achieved experiences are described. This process flow differs from the fabrication process carefully explained in Section 5.1, since the in- and outlet holes were etched during the cleanroom processing, and thus before the anodic bonding. The process flow for the top wafer containing channels is altered considerably due to this difference, but it does not affect the fabrication method for the bottom electrode wafer. A summary of the process flow of the top wafer with etched inlet holes is shown in Fig. 5.10 for the chip cross section marked in Fig. 5.1. A more detailed process flow including a full step by step processing list applicable in the MIC cleanroom facilities is enclosed in Appendix C. Assuming that the machines will be repaired and everything works perfect, this process takes approximately one and a half week to complete.

5.3. ETCHING INLET HOLES



Channel wafer with HF etched inlet holes (top wafer)

Figure 5.10: Summary of the planned process flow with etched in- and outlet holes, depicted at the cross section shown from above in Fig. 5.1. Only the processing of the top wafer is illustrated, since the process flow of the bottom wafer containing electrodes is unchanged and shown in Fig. 5.2. The assembled chip is sketched at the bottom.

5.3.1 Process flow

The alternative process flow for the top wafer consists of two parts. First the inlet holes are made by processing the outward wafer side, and secondly the channels are etched during processing of the inward wafer side. Since the holes are etched all the way through the wafer using a timed etch, it is important to measure the exact wafer thickness from the beginning as it may vary within a range of $100 \,\mu\text{m}$.

Processing of outward wafer side

A layer of 1000 nm amorphous silicon was deposited on the Pyrex surface under the same conditions as explained in Section 5.1. The a-Si layer combined with a thick layer of photoresist acted as etch mask during the long hydrofluoric etch of the inlet holes.

Within two hours after the silicon sputter deposition, a $9.5 \,\mu\text{m}$ thick layer of positive photoresist was spun onto the wafer, which was subsequently prebaked on a 90°C hotplate for 3 min. The wafer was then left for at least 1.5 hours to let the remaining solvent evaporate. Mask number 3 (Fig. 4.7) was used during exposure, which was carried out at hard contact for 50 s. Normally such a long exposure would be performed in several steps, for instance by turning off the light a couple of seconds for every five seconds of exposure. This is done in order to prevent the resist from heating up and getting softer, thereby resulting in less sharply defined contours. However, the holes defined in this process are hundreds of micrometers wide, and a less sharp edge is thus insignificant. The resist was subsequently developed for 4.5 minutes.

After development, the a-Si layer was etched within 40 min and in the meantime, the inward wafer side and wafer edges were covered with blue tape to protect against the later HF etching. Etching of the amorphous silicon layer was done in the same solution as described in Section 5.1 for 5 min, and the holes were carefully inspected to ensure the complete removal of all a-Si in the hole pattern. As shown in Fig. 5.11, minor holes in the etched a-Si film due to impurities or bobbles in the thick photoresist layer were occasionally observed. After the HF etch, this generated some minor holes in the Pyrex wafer surface as well, however, these unintended holes would never be able to cause a through-etch of the wafer as a result of the significantly reduced etchant flow.



 $350 \mu m$

Figure 5.11: Micrographs of the etched amorphous silicon layer in back-illumination. To the left a well defined hole in the etch mask is shown, and to the right some minor particles or bobbles in the photoresist layer has caused some additional minor holes in a-Si layer. However, these small holes do not result in extra holes penetrating the entire thickness of the wafer.

In the next step, the alignment marks were covered with blue tape before the long glass etch to avoid that they turn into craters. The resist was hard-baked for 25 min in a 120° C oven and within less than two hours later the HF etching was carried out in the same way as explained in connection with the channel etch. It took approximately 2.5 hours to etch the holes, and it was important that they were not etched all the way through the wafer in this step, as explained below.

Finally, the blue tape was removed in acetone, and the photoresist was dissolved by applying ultrasound to an acetone bath. It could also be necessary to clean the wafer in a Piranha solution before proceeding by processing the opposite wafer side.

5.3. ETCHING INLET HOLES

Processing of inward wafer side

At the inward wafer side, the channels were defined and etched. The process is very similar to the process of the channel wafer outlined in Section 5.1, whence only the main changes will be described here.

As before, a thin 100nm amorphous silicon layer was sputter deposited on the wafer substrate, and the negative photolithography process was performed. This time, the outward wafer side was not covered with blue tape. During the following a-Si etching (Section 5.1.2), both the thick outward silicon layer and the channel pattern in the thin silicon film were etched simultaneously. This etch step lasted approximately 2.5 min and was easily inspected, since the channels became transparent.

Next, the wafers were hard baked on a 120°C hot-plate for 2 min before HF etching of the channels. In this etch process, the channels were etched from one side while the holes were getting deeper from the other side until the holes had been etched all the way through the wafer. Finally, acetone was used to remove the photoresist layer and prior to the bonding process, the wafer was cleaned in Piranha.

5.3.2 Challenges

Much effort was put into the process flow outlined above, and the fabrication almost yielded the intended result. In the following, it is explained how different parts of the process had to be adjusted during fabrication, and which process steps that were successfully tested.

It should also be noted that the process flow was changed after the first iteration. Deposition of amorphous silicon on both sides of the wafer in the same process step was attempted at the beginning of the fabrication, but it was not possible to efficiently protect the thin a-Si layer during the outward wafer processing. In the second iteration, the processing of the two wafer sides was then divided into separate processes, as explained above.

Calibration of HF etch rate

The combination of the etching processes relies on the exact knowledge of the Pyrex etch rate, since the hole etching should be stopped when exactly two times the wanted channel height of the total wafer thickness remained. Logically, an under-etching of the holes was undesirable, since there would be no resulting connection between channels and holes, but also an over etching would be a disadvantageous for reasons that will become clear in the following.

A test of the hole etching process showed that the etch rate was highly dependent on parameters such as the hole diameter and the stirring velocity. Initially, an etch rate of $3.4 \,\mu\text{m/min}$ was assumed, but it turned out that the holes were not even close to being etched through the wafer (550 μ m) after more than four hours of etching at the highest possible stirring velocity, which should be sufficient to etch a hole one and a half times the wafer thickness. The hole size defined by the mask was only 100 μ m, which may have been too narrow to ensure a regular flow of etchant within the hole. The diameter was deliberately chosen that small to avoid a final upper hole diameter larger than the inner diameter of the O-rings (1.6 mm) sealing the fluidic connections at inand outlets of the chip holder (Chapter 6). Since the etch is isotropic, the upper hole diameter will then at least be the size of two times the hole depth plus the original hole diameter, i.e. for a channel of height 30 μ m the diameter will become approximately $2 \times (550 \,\mu\text{m} - 30 \,\mu\text{m}) = 1.04 \,\text{mm}$ plus the hole diameter defined by the photolithographic mask.

To increase the etch rate, a new mask was tried out with hole diameters of $350 \,\mu\text{m}$, corresponding to a final upper hole diameter of approximately 1.4 mm. This hole size resulted in a vertical etch rate of $3.40 \,\mu\text{m}/\text{min}$ at the highest possible stirring velocity. Another conclusion that can drawn on the basis of the performed etch tests concerns the etching isotropy. It became apparent that the horizontal etch rate (along the wafer surface) was higher than the vertical etch rate, possibly due to the increased flow of etchant near the surface. The approximate value of the horizontal etch rate was $4.1 \,\mu\text{m}/\text{min}$.

Due to the aforementioned problems regarding amorphous silicon deposition, the performed etch tests were combined with adhesion and resistance tests of the amorphous silicon layer, thereby prolonging the calibration process significantly.

Current status

Having determined the etch rate and successfully controlled the etching of holes and channels in separate wafers, the next step was to try out the whole process, combining etching of channels and holes in the same wafer. Processing of the outward wafer side went well, but a problem occurred through the final etching of the channels, where it turned out that the adhesion of the thin amorphous silicon film to the substrate was too weak to sustain more than a few minutes in the HF bath.

A closer examination of the inward wafer side, before deposition of the thin a-Si layer, revealed vague whitish spots with a diameter around one millimeter. A micrograph of the surface is shown in Fig. 5.12. Measurements with the Dektak profiler showed a surface roughness of approximately 100 nm across the spots, but due to tensions in the wafer it was not possible to decide whether the roughness was caused by small material depositions or a arbitrary removal of the substrate. The spots could indicate that some treatment during the outward wafer processing affected the inward wafer surface and resulted in the poor adhesion between amorphous silicon and substrate.

If the spots were caused by an unintended material deposition, it could be possible to clean them. Another Piranha cleaning was attempted without result, and also an RCA cleaning was performed. In the latter cleaning process, the wafers are exposed to a solution of $H_2O:NH_4OH:H_2O_2$ in the ratio 100:18:25, which is heated to 70°C and left for 10 min. Also this treatment was in vain.

One possible explanation of the cause to the formation of spots could be the first short treatment in 5% HF solution, where the naturally grown oxide layer on the outward wafer surface is removed from the thick amorphous silicon layer prior to the photoresist deposition. In this process step, also the inward wafer side is exposed to the hydrofluoric solution, which could damage the surface and result in the poor adhesion of the subsequently deposited thin amorphous silicon layer. If the resist is deposited immediately after



Figure 5.12: Micrographs of the vague spots on the inward wafer surface after processing of the outward wafer side. The diameter of this spot is approximately 1.3 mm as shown to the left. To the right, a magnification of the spot surface is depicted.

the a-Si deposition, the process step of HF rinsing can be avoided. However, this was not done due to the mentioned machine breakdown.

5.4 Summary

Although the fabrication process proved extremely challenging and laborious, functional chips were successfully fabricated, and moreover, transparent channels with asymmetric electrode arrays were realised.

Following several unproductive attempts, the original plan of etching holes was abandoned due to a permanent machine breakdown. However, apart from this force majeure wafer processing was successfully carried out and a complete process flow, including calibrated hole etching rates, was developed, which will be directly applicable if the necessary machines are available. Caused by the inability of the hole etching step to be integrated in the process flow holes were drilled instead. Fortunately, this did not seem to cause trouble during flow measurements with respect to potential clogging of the microfluidic channels.

Overall, the bonding method proved effective, yet some chips leaked along one of the sides due to the design with electrodes close to the chip edge. In connection with this, it was observed that the bonding worked for a larger electrode spacing than estimated in the design phase.

Chapter 6

Measurement setup

To test the pumping ability of the fabricated devices, tubes and wires were connected to the chip and a measurement setup was constructed. Electrical connection to the contact pads and sealing of the outer tubing to the micro channel were achieved using a special manufactured chip holder presented in the first section. A circuit of tubes and valves connected to the chip holder was used to direct and control the liquid avoiding undesirable pressure differences and contamination of the chip. In the last section, the final setup used for velocity determination within the micropump is described. Before this complex setup was utilized, other tests of the micropump chips were carried out. The hydraulic resistance of the etched fluid channel was determined, and impedance measurements were performed for various electrolytes. A different instrumentation and liquid circuit was necessary for each type of measurement and in the following, the individual setups are outlined. All specifications of the utilized instruments are listed in Appendix D. Results of the measurements are shown in Chapters 7 and 8.

6.1 Chip holder

The chip holder shown in Fig. 6.1 consisted of two 6 mm thick PMMA polymer plates clamped around the chip, with a window cut out in both top and bottom plate to give access to the channel sections containing electrodes and velocity detection ruler lines. Above the in- and outlet holes in the glass chip, thin channels with diameter 0.9 mm were drilled and directed to the side of the top PMMA plate, where threads were made for the fittings between chip holder and outer latex tubes. Flat O-rings between the chip and the PMMA plate sealed the liquid passage from microfluidic channel to drilled channel. Choosing flat O-rings minimized the dead-volume of the fluidic connection to the chip.

Electrical contact was obtained using spring loaded contact pins, which made it easy to change the chip in the holder and avoided epoxy gluing or soldering of electrical wires onto the thin metal film. The inner wires of thin coax cables were soldered onto the contact pins, and a plate was constructed to fasten the cables avoiding undesired pulling in the contact pins. This plate was glued vertically onto the top PMMA chip holder plate close to the contact pins, and holes were drilled for the cables, which were subsequently



Figure 6.1: Chip holder used for all experiments. The outer tubing was connected to the microfluidic channel with a fitting screwed into the upper PMMA plate. A drilled channel directed the liquid through the PMMA, and an O-ring sealed the connection to the channel. Spring loaded contact pins were pressed against the electrode pads on the chip, and the inner wire of thin coax cables were soldered to the pins. A holder plate was constructed for the cables to avoid undesired pulling in the contact pins.

attached to the plate holes with epoxy. The shields of the coax cables terminated on the plate, and since experiments demonstrated the importance of short-circuiting the shields to avoid inductive effects from the long cables, aluminum was chosen as plate material. No difference between thin and thick coax cables was observed, so thin cables were chosen in order to obtain a more flexible chip holder construction.

During the experiments, the chip holder was fastened to a small metal tripod, where also the outer liquid circuit with latex tubes and valves was attached. Immediately after drilling of in- and outlet holes in the fabricated microchip, the chip was mounted in the chip holder and flushed with milli-Q water to remove possible drilling dust from the channel.

Finally, it may be noted that a much thinner aluminum bottom (3mm) was also constructed for the chip holder, in order to minimize the working distance from the bottom. This makes for instance μ -PIV possible, where only a few millimeters are allowed between sample and microscope.

6.2 Instrumentation

6.2.1 Setup for determination of hydraulic resistance

The hydraulic resistances of the etched channels were determined using the setup shown in Fig. 6.2. This was an automated setup for measuring Q-p characteristics of a fluidic device. Using a Labview program, two electroactuated valves were regulated to create a number of pressure differences across the device. With a data acquisition card in connection with the Labview program, a number of variables in the fluidic circuit were sampled at 1 Hz



Figure 6.2: a) The fluidic setup used to measure hydraulic resistance of the fabricated microfluidic channels. b) A magnification of the chip holder positioned between the two sensors measuring the pressure difference across the device for a given flow rate. This picture corresponds to the framed part of the diagram in Fig. 6.3. It may be noted, that the narrow side channel was plugged, and the resistance was measured only for the channel, which was a part of the pump loop.



Figure 6.3: Sketch of the fluidic circuit used for hydraulic resistance measurements. The flow was driven by external nitrogen pressure, controlled via two electroactuated valves V_1 and V_2 . The pressure difference across the microchip was measured by the pressure sensors p_1 and p_2 and the flow rate was determined from the balance output m. The dashed line around the microchip and pressure sensors corresponds to Fig. 6.2b.

during the measurements and stored in a data file [18]. The Labview program is shown in Appendix E.

The fluidic circuit is sketched in Fig. 6.3. The flow was driven by pressurized liquid reservoirs, and the pressure difference across the fluidic device was controlled by regulation of the external N₂ pressure. By opening each of the two electroactuated values V_1 or V_2 , the pressure was increased or decreased, respectively. Note, that the values were never

open simultaneously. Two pressure sensors on each side of fluidic device measured the pressure difference, and these values were stored in the data file as p_1 and p_2 . The liquid was directed from the fluidic device into a bottle placed on a balance, feeding the mass m into the data file as a measure of the flow rate Q through the device. The last variable stored in the data file was the elapsed time t.

Matlab was used for plotting the resulting p-Q characteristics from the acquired data file and estimating the hydraulic resistance from the slope, see Eq. (2.18). This program is shown in Appendix E.

6.2.2 Impedance measurement setup

An electrical characterization was performed for micropumps containing both air and various electrolytes. Using an Impedance Analyzer, impedance spectra were obtained at a given oscillation voltage over a series of frequencies. The oscillation voltage could be specified within a range of $10 \,\mathrm{mV_{rms}}$ to $1 \,\mathrm{V_{rms}}$, thus making it possible to measure in both the Debye–Hückel limit ($\ll 25 \,\mathrm{mV}$) and into the strongly nonlinear high-voltage regime.

The Impedance Analyzer was constructed to perform four-point measurements in order to minimize the effect of contact resistance on the impedance values. Short circuiting of adjacent contact pins on the contact pads made it possible to let a large current flow between the outer pins, while the measurement was performed across the inner pins. The resistance of the Impedance Analyzer was very high between the inner pins, thus the current flowing through these probes was negligible. Consequently, the impedance measurement or current-voltage curve was more accurate than an ordinary two point measurement would have been. Data was acquired at 400 different frequencies evenly distributed on a logarithmic scale within the specified measurement interval. The integration time at each data point was adjusted in order to eliminate measurement uncertainties. The measured output spectrum was exported to a data file containing columns of frequency, absolute impedance and phase, after which the data was analyzed and plotted using Origin.

Before actual microchip measurements were carried out, a compensation measurement was obtained to correct for possible inductive, capacitive and resistive effects occurring in various parts of the external electronic circuit. This compensation was a built-in function for cables of length 1 m. Utilizing this function decreased the maximum range of frequencies that could be analyzed to an interval of 100 Hz to 15 MHz. The compensation measurement was performed for an open circuit, i.e., the chip holder was measured without a chip mounted, but instead a short circuiting of the contact pins was created by a thick piece of aluminum. Subsequently, all impedance spectra were corrected according to this compensation measurement.

In Fig. 6.4 the simple setup is shown. After mounting the chip in the chip holder, proper electrical contact between each of the two pairs of electrodes was ensured by using a multimeter. A syringe with a $0.45 \,\mu\text{m}$ filter was used for injecting the electrolyte into the microchannel. Subsequently, the three in- and outlets were closed and the chip was ready for characterization.



Figure 6.4: The setup for impedance measurements only consisted of the chip holder electrically connected to the Impedance Analyzer via the four contact pins. The liquid was manually pumped through the microchannel using a syringe. During measurements, the three in- and outlets could be closed in order to minimize fluid motion.

6.2.3 Measurement setup for flow velocity determination

The final setup was constructed to detect flow generated by the electrodes in the microfluidic channel of the fabricated chip. The flow was detected in the channel section without electrodes, as explained in Chapter 4, by introducing fluorescent beads into this part of the channel and detect the flow with a camera attached to a stereo microscope. Pictures of the moving beads were then stored at exact time intervals making a subsequent determination of the flow velocity possible.

The fluidic circuit controlling the flow of electrolytes and beads during the experiments is shown in Fig. 6.5, where both a photograph of the actual circuit and a corresponding schematic drawing are presented. The big valves with four in- and outlets only allow the fluid to pass from one tube to another along the sketched turnable angle. Through the right valve the beads were loaded into the channel, and also the electrolyte used for subsequent flushing was led into the system this way. These solutions of beads were manually injected into the channel using syringes, and the last outlet from the right valve was used to let air bobbles out of the syringe tip before flushing the liquid into the microchannel. The big four-way value to the left was used as part of the outer pump loop. Both beads and electrolyte were flushed out of the system through this valve (bottom inlet), and electrolyte was flushed into the system and over the electrodes from the left inlet of the valve. The three minor valves were not strictly necessary to complete the fluidic circuit, but were added in order to obtain better control with the pressures around the circuit. The deadvolume of these valves was small compared to the bigger four-way valves. Closing the small valves thus minimized the compressibility of the fluid around the circuit and made it easier to control the spreading of fluorescent beads.

The potential difference between the thin and thick electrodes of the asymmetric array was obtained using the internal sinusoidal input signal of a Lock In Amplifier in connection with a current amplifier, which delivered the current necessary to maintain the specified



Figure 6.5: Liquid circuit used for determination of the generated fluid velocity in the microchip. a) is a photograph of the setup and b) shows the corresponding schematic circuit. Beads and electrolytes were injected into the microfluidic channel through the right four-way valve, and waste exited the liquid circuit through the left valve. Electrolyte was also flushed over the electrode area through the left four-way valve. The three minor valves were added to the circuit for better control of pressure differences within the circuit.

voltage difference. By default, the current amplifier also amplified the voltage three times. Flow generation was expected for driving voltages in the range 1-2 $V_{\rm rms}$, thus the Lock-In amplifier output voltage amplitude needed to be 1/3 of this range. However, in this low output voltage regime the Lock-In Amplifier signals might not be completely noise free. In order to avoid these low output signals, the voltage was divided 1:3 before the current amplification. Consequently, the micropump input voltage amplitude corresponded to the value specified on the Lock-In Amplifier. The electrical circuit used to generate flow is shown in Fig. 6.6.



Figure 6.6: Electrical circuit devised to provide the necessary voltage difference across the fabricated micropump. The input signal was generated by a Lock-In Amplifier and the voltage drop was divided 1:2 between the resistances $R_s = 2.05 \text{ k}\Omega$ and $R_l = 4.02 \text{ k}\Omega$. Subsequently the input signal was sent through a current amplifier, which by default also amplified the voltage three times. The impedance output from the micropump was measured by the Lock-In Amplifier across a small resistance $R_I = 51.7 \Omega$ coupled in series with the chip.

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The input signal V_{in} was coupled to the electrode array, and the output signal was measured across a small resistance R_I coupled in series with the micropump. On the Lock In Amplifier, the output amplitude V_{out} and the phase θ relative to the input signal were displayed. From the in- and output signals, the absolute value |Z| of the impedance Z at the given frequency may be calculated as

$$|Z| = \frac{V_{\rm in}}{I} = R_I \frac{V_{\rm in}}{V_{\rm out}},\tag{6.1}$$

where I is the current through the micropump and resistance R_I .

The velocity of the injected beads was detected utilizing a stereo microscope focused at the detection area of the channel, see Fig. 6.5. A camera was attached to the microscope and pictures were acquired within certain time intervals down to around 200 ms. The sampling frequency depended on bead flow velocity and light intensity. The fluorescent light was rather weak and a shutter time of approximately 60 ms was necessary to obtain clear pictures of the moving beads. It should be noted that by using fluorescence light, undesirable sample heating was avoided.

Chapter 7

Electrical characterization

As a first step in the measurement phase of the present project, the electrical characteristics of the micropumps were systematically investigated. Utilizing the impedance setup described in Section 6.2, spectra of the absolute impedance and corresponding phase were measured over a range of frequencies. Chips with different electrode translation periods were studied and the effect of altered ion density was examined, i.e., the electrolyte conductance was varied. Furthermore, two different electrolytes were employed, having dissimilar ion sizes and thereby unequal diffusivity. These electrolytes are presented in the first section. The frequency spectrum was additionally swept for different voltages within the range of $10 \,\mathrm{mV_{rms}}$ to $1\mathrm{V_{rms}}$, making it possible to investigate the transition from the Debye–Hückel limit ($\ll 25\mathrm{mV}$) into the nonlinear high voltage regime. Section 7.2 begins with an outlining of the measurement procedure and a presentation of general observations regarding the system. Next, the measured spectra are shown, and finally, the equivalent diagram described in Chapter 3 is discussed.

7.1 Electrolytes

Two electrolyte types, borax buffer and diluted KCl, in various concentrations have been used during the experiments. In Tables 7.2 and 7.1 conductance measurements of these solutions are shown. Since the conductivity of an electrolyte strongly depends on temperature through the ionic mobility, Eq. (2.23), the solution temperature has been measured simultaneously with the conductance.

For the present experiments, KCl was chosen for two reasons. The constituting ions are both monovalent and have approximately the same size. Thus, the theory of Chapter 3, considering liquid motion above an electrode array for an electrolyte containing monovalent

KCl	0.1 mM	$0.2\mathrm{mM}$	$0.3\mathrm{mM}$	$1\mathrm{mM}$	$0.1\mathrm{M}$
Conductance, $\sigma [10^{-3} \mathrm{S/m}]$	1.43	2.76	4.08	13.5	1194
Temperature, T [°C]	23.2	25.2	22.8	22.9	22.5

Table 7.1: Conductances measured for the used KCl solutions.

borax	0.1 mM	$0.5\mathrm{mM}$	$1\mathrm{mM}$	$10\mathrm{mM}$	40 mM
Conductance, $\sigma [10^{-3} \mathrm{S/m}]$	1.79	8.34	16.1	141	482
Temperature, T [°C]	22.6	22.8	22.4	22.8	22.9

Table 7.2: Measured conductances of the applied borax buffer solutions.

ions with equal diffusivity, is applicable. Secondly, the work of Studer *et al.* [3] is based on electrolytic solutions of KCl, which makes a direct comparison with these results possible. The KCl salt dissociates in water as

$$\mathrm{KCl} \quad \to \quad \mathrm{K}^+ + \mathrm{Cl}^-. \tag{7.1}$$

As a contrast to the equal sized ions in a KCl solution, borax buffer was chosen to be the second electrolyte used for the experiments. This is a well characterized buffer solution [18] containing small positive Na ions and larger negative ions. The molecular formula of borax buffer in crystalline form is $Na_2B_4O_7 \cdot 10 H_2O$. When the crystal is exposed to water it dissociates as boric acid and the conjugate base,

$$Na_2B_4O_7 + 7H_2O \rightarrow 2H_3BO_3 + 2B(OH)_4^- + 2Na^+,$$
 (7.2)

where the acid reacts as $H_3BO_3 + H_2O \rightleftharpoons H_2BO_3^- + H_3O^+$.

Milli-Q water was also utilized during the experiments. The system was flushed with water to clean the channel and tubes for ions, and also a few impedance spectra were obtained with pure water in the microfluidic channel. The conductance of milli-Q water was measured to $\sigma = 0.05 \times 10^{-3} \,\text{S/m}$ at 23°C.

7.2 Impedance

7.2.1 Impedance measurement procedure

After the compensation measurement of chip holder and cables, described in Section 6.2, a microchip was mounted in the chip holder, and the channel was filled with liquid. Approximately 1 mL water or electrolyte was pumped through the channel before all openings were shut off by closing the valves in order to minimize liquid motion during the following impedance measurements. For comparison, the total volume of the channel was $1.3 \,\mu$ L, and the remaining tubing volume between channel and valves was approximately 0.1 mL.

During the preliminary measurements, two general observations were made regarding system flushing and the examined frequency interval. It was seen that the impedance curve changed with time, depending on the liquid contained in the channel. The effect was clearest for milli-Q water and depended on how the channel had been flushed and filled. Apparently, the change was lesser for milli-Q water when the entire system had been flushed thoroughly. In Fig. 7.1 a number of impedance curves have been measured over a time sequence for a system, which has been flushed and filled with milli-Q water after containing 1 mM KCl. Fig. 7.1a shows the curves as a function of frequency, and Fig. 7.1b depicts the time development of the impedance at given frequencies. The latter curves



Figure 7.1: a) Spectra of the impedance as a function of frequency for a micropump containing milli-Q water measured over a time interval of 30 min. b) The decreasing impedance is plotted for a number of frequencies as a function of time and fitted linearly.



Figure 7.2: The slopes of the linear fit in Fig. 7.1b are plotted with red circles. A cleaner system containing milli-Q water have been investigated correspondingly and is plotted with black squares. Another two series obtained for systems containing KCl solutions of 1 mM and 0.1 mM shows how the impedance change over time is much less for these electrolytes.

have been fitted linearly and the slopes are plotted as a function of the corresponding frequencies in Fig. 7.2 (marked with red circles). Here, another two time series have been shown for systems flushed with milli-Q water and subsequently filled with 0.1 mM and 1 mM KCl solutions, respectively. Additionally, an extra time series for milli-Q water has been measured. This series was obtained for a system cleaned more carefully than the one first described and has been plotted with black squares.

From Fig. 7.2 it is seen that the change of impedance over time was largest for low frequencies and almost zero for high frequencies. Furthermore, it is seen that the impedance generally decreased when the system contained milli-Q water, while a slightly increasing impedance was observed for the electrolytic solutions. However, the change for the electrolytic solutions was much smaller compared to the system filled with milli-Q water. Finally, it may be noted that the impedance change is smaller for the higher electrolyte concentration.

The above shown measurements indicate that an amount of ions may remain in the system after flushing with milli-Q water, since subsequently the resistance of the liquid slowly decreases. Conversely, the slightly increasing resistance for an electrolyte-filled system suggests that a small amount of ions diffuses out of the electrode area in the channel. Over 1 min the small ions of KCl may spread out over an area of approximately $0.12 \,(\text{mm})^2$.

Since the variation of impedance measurements with milli-Q water in the channel was rather large and depended on the previous system contents, it was decided only to use milli-Q water for cleaning purposes, and electrolytic solutions for the actual electrical characterization of the system. The change of impedance was largest right after the channel was filled with liquid and then became smaller. For the electrolytes the impedance was stable after 15 to 20 min, and consequently, the impedance spectra were all measured 20 min after filling electrolyte into the system. Between each measurement, the system was carefully flushed with milli-Q water and the impedance spectrum was checked before the new electrolytic solution was filled into the channel. When the electrolyte was pumped into the system also the tubing volume between the valves was filled to avoid diffusing effects on the electrolyte concentration.

Regarding the frequency interval for the impedance measurements, it was observed that some combinations of frequency and voltage led to damaging of the electrodes. When the spectrum was swept at $1 V_{\rm rms}$, discontinuities in the impedance were observed in the low frequency regime. In Fig. 7.3 two spectra are shown for a chip containing milli-Q water. First, a spectrum was obtained at $1 V_{\rm rms}$, and as the frequencies were swept from 100 Hz and upwards the discontinuities appeared. Obtaining a spectrum at $100 \,\mathrm{mV_{rms}}$ to avoid further damaging of the electrodes subsequently showed a clearly lowered impedance. This reduced impedance level was permanent. The electrode damaging might be due to electrochemical reactions at the electrode surfaces. At very low frequencies, the external voltage



Figure 7.3: An example of electrode damage. The two impedance spectra were measured for a chip A75 containing milli-Q water. First, a spectrum was obtained at $1 V_{\rm rms}$ by sweeping the frequencies from 100 Hz and upwards. Discontinuities were observed for low frequencies before a stable impedance level was reached. Measuring a spectrum at 100 mV_{rms} afterwards indicated that the impedance level was permanently lowered.

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corresponds to DC voltage, where electrode reactions are likely to occur. Consequently, all impedance spectra were obtained by sweeping from high frequencies towards the low frequency area, and for oscillation voltages of $1 V_{\rm rms}$, the full spectrum was not measured.

7.2.2 Results of the impedance measurements

Before the results are presented, a short introduction to the general form of the impedance spectrum is given. The spectrum shown in Fig. 7.4 is representative for the qualitative shape of the absolute impedance measurements obtained for the micropumps.



Figure 7.4: Representative measurement curve obtained for chip A50 containing 0.1 mM KCl at 10 mV. Two characteristic resistances have been indicated, R_{bulk} , referring to the resistance of the bulk electrolyte, and R_{wires} , referring to the resistance of wires and electrodes. The marked characteristic frequencies corresponds to the 1/RC times of the equivalent circuit depicted in Fig. 7.5.

As indicated in the figure, two characteristic frequencies ω_D , see Eq. (3.19), and ω^* and two resistances R_{bulk} and R_{wires} may be used as a guidance during the presentation and discussion of the measured impedance spectra. These parameters might be explained on basis of the introduced equivalent diagram in Section 3.1. Eq. (3.4) can be simplified as follows:

$$Z = 2R_{\rm pad} + \frac{1}{p} \left\{ R_w + R_n + \left[\left(\frac{R_{\rm gap}}{2} + \frac{1}{i\omega C_n} + \frac{1}{i\omega C_w} \right)^{-1} + i\omega C_\infty \right]^{-1} \right\}$$
(7.3a)

$$= 2R_{\text{pad}} + \frac{1}{p} \left(R_w + R_n \right) + \left[\left(\frac{R_{\text{gap}}}{2p} + \frac{1}{i\omega pC_n} + \frac{1}{i\omega pC_w} \right)^{-1} + i\omega pC_\infty \right]^{-1}$$
(7.3b)

$$= R_{\text{wires}} + \left[\left(R_{\text{bulk}} + \frac{1}{i\omega C_1} \right)^{-1} + i\omega C_2 \right]^{-1}.$$
(7.3c)

In the last equation the following notation has been utilized:

$$R_{\text{wires}} = 2R_{\text{pad}} + (R_w + R_n)/p, \qquad (7.4a)$$

$$R_{\rm bulk} = R_{\rm gap}/(2p),\tag{7.4b}$$

$$C_1 = p C_n C_w / (C_n + C_w),$$
 (7.4c)

$$C_2 = pC_{\infty}.\tag{7.4d}$$

Based on the considerations of Chapter 3 (Section 3.1), the components of the equivalent diagram may roughly be estimated from the following expressions.

$$R_{\rm pad} = \frac{\rho}{h} \frac{\rm length}{\rm width},\tag{7.5a}$$

$$R_w = \rho \, \frac{w_{\rm el}/2}{hl_E}, \qquad R_n = \rho \, \frac{w_{\rm el}/2}{hl_e}, \tag{7.5b}$$

$$R_{\rm gap} = \frac{3}{\sigma w},\tag{7.5c}$$

$$C_w = w l_E C_0, \qquad C_n = w l_e C_0. \tag{7.5d}$$

Above, h is the electrode thickness, ρ the metal resistivity, σ the electrolytic conductivity, w the width of the channel and $w_{\rm el}$ the length of the electrodes in the array. l_e , l_E , l_g and l_G are the electrode widths and spacings of the electrode array, given in Table 4.1 for the three different translation periods. The unspecified length and width in Eq. (7.5a) are determined from the dimensions of wires connecting the electrode array with the contact pads. These wires consists of sections with varying length and width, see Fig. 4.2. C_0 is the double layer capacitance given in Eq. (3.2). Finally, the capacitance C_{∞} is estimated as a parallel coupling of the capacitances between adjacent electrodes in the array. The capacitive coupling is both through the electrolyte of permittivity $\epsilon_{\rm electrolyte}$ equal that of water, and through the glass bottom and sides of the channel with permittivity $\epsilon_{\rm glass}$.

$$C_{\infty} = \epsilon_{\text{electrolyte}} \left[\frac{wl_e}{l_g} + \frac{wl_e}{l_G} \right] + \epsilon_{\text{glass}} \left[\frac{(2w_{\text{el}} - w)l_e}{l_g} + \frac{(2w_{\text{el}} - w)l_e}{l_G} \right].$$
(7.6)

Parameters used for estimating the outlined components of the equivalent diagram are listed in Tables 7.3 and 4.1.

In Fig. 7.5 the simplified equivalent diagram corresponding to Eq. (7.3c) has been drawn. Returning to Fig. 7.4, the four components of the electrical circuit corresponds to the characteristics of the impedance curve. The middle level around 1500Ω corresponds



Figure 7.5: Simplified equivalent circuit for the entire electrode array. It consists of the bulk resistance R_{bulk} of the electrolyte, the two capacitances of the Debye layer and the electrodes, C_1 and C_2 , respectively, and the resistance of the wires R_{wires} .

Debye length	$\lambda_{\rm D} = 30{\rm nm}$
Double layer capacitance	$C_0 = 0.024 \mathrm{F/m^2}$
Conductance (0.1mM KCl)	$\sigma = 1.43\mathrm{mS/m}$
Resistivity (Pt)	$\rho = 10.6 \times 10^{-8}\Omega\mathrm{m}$
Permittivity of electrolyte	$\epsilon_{\rm electrolyte} = 80 \epsilon_0$
Permittivity of Pyrex substrate	$\epsilon_{\rm glass} = 5 \epsilon_0$
Electrode thickness	$h = 400 \mathrm{nm}$
Channel width	$w = 967 \mu\mathrm{m}$
Electrode length	$w_{\rm el} = 1300\mu{\rm m}$

Table 7.3: Summary of parameters used for the calculation of the equivalent components listed in Table 7.4.

to the resistance R_{bulk} of the bulk electrolyte between the electrodes. For very high frequencies, the impedance becomes nearly zero, but not completely due to the resistance R_{wires} of electrodes and wires connecting the electrode array with the electrical contact pads. The two capacitors represents the double layer capacitance C_1 and the capacitance of adjacent electrodes in the array C_2 . In connection with R_{bulk} these capacitors give rise to two characteristic frequencies of the system, ω^* and ω_D , differing approximately a factor 1000. The former frequency corresponds to the 1/RC frequency for a series connection of R_{bulk} and C_1 , and the latter frequency corresponds to the 1/RC frequency for a parallel coupling of R_{bulk} and C_2 . ω^* might be interpreted as the resonance frequency of the system, while ω_D is the Debye frequency Eq. (3.19), where the ions no longer are able to follow and screen the external potential.

In addition to the spectra of the absolute impedance, the corresponding phase spectra are presented. Typically, the phase is almost zero at frequencies for which the impedance corresponds to R_{bulk} , and tends towards -90° C for higher and lower frequencies, where the capacitive effects change the impedance.

The entire equivalent diagram is further discussed in a later section.

Variation of the translation period

Before in- and outlet holes were drilled in the fabricated chips, impedance spectra were obtained for the different types of chips, i.e., for micropumps of different translation periods. The fabricated translation periods were 100 μ m (A100), 75 μ m (A75) and 50 μ m (A50) with electrode spacings and gaps as specified in Table 4.1. The spectra are shown in Fig. 7.6.

The absolute value of the impedance, Fig. 7.6a, became larger for an increased translation period. Especially in the low frequency regime, the difference between the chips was significant. In the high frequency limit, the lowest measured impedance value was $|Z| = 637 \Omega$. For chip A50, the absolute impedance was constant over the lower part of the frequency spectrum, while A75 showed a divergence for low frequencies and A100 diverged even faster. This tendency was also reflected in the phase plotted in Fig. 7.6b. Chip A50 had zero phase in the lower half of the frequency spectrum, while the phase of



Figure 7.6: Impedance spectra measured for micropumps of three different translation periods before holes were drilled in the chips, i.e., for channels containing air. The oscillation voltage was $100 \,\mathrm{mV_{rms}}$.

A75 was slightly negative and the phase of A100 changed significantly towards negative values. All of the samples had a phase of -90° C for the highest frequencies.

The spectra obtained for the air filled chips can not directly be discussed on the basis of the previously described equivalent diagram, which applies for electrolytes in the vicinity of the electrodes. It should rather be compared with a resistance and a capacitance coupled in parallel, and this is discussed further in a subsequent section.

Fig. 7.7 shows impedance spectra for channels of varying translation period containing 0.1 mM KCl solution. The shapes of the curves were more consistent in this case. A nearly regular scaling of the absolute impedance spectra, Fig. 7.7a, was observed for different translation periods, where the impedance was increased with increasing electrode spacing. Apparently, the characteristic frequencies of the system were rather similar for all spectra. In the low frequency end, the impedance was increasing for all translation periods, and in the high frequency limit all spectra tended towards the same constant value of $|Z| \rightarrow 30 \Omega$. The corresponding phase spectra, Fig. 7.7b, were almost coinciding, only a slight deviation was observed for chip A50 in the limits of the highest and lowest frequencies.

Based on the previously outlined equivalent diagram, a scaling of the translation period corresponds to a scaling of the capacitance areas of both C_n , C_w and C_∞ and a scaling of the plate distance of C_∞ , while the gap resistance R_{gap} remains unchanged. Utilizing Eq. (7.4) and keeping in mind how the number p of electrode pairs per array differs for the three geometries, it is seen how R_{bulk} increases with increasing translation period. C_∞ is estimated as $C \sim \epsilon$ area/length, where the area scales with the width of the narrow electrode and the length is the electrode spacings. Since the three geometries are designed by multiplying the geometry A50 by 1.5 and 2, respectively, all distances within the same electrode array scale uniformly. Consequently, C_∞ is equal for all translation periods and C_2 scales with p. Estimating the RC frequency from R_{bulk} and C_∞ then results in the same frequency - p is divided out. C_n and C_w only depend on the electrode area and vary for the three geometries. Multiplying with p nearly outbalances this difference. Thus, the RC frequency differ for the three electrode arrays due to the change in bulk resistance.



Figure 7.7: Impedance spectra obtained for micropumps of three translation periods containing $0.1 \,\mathrm{mM}$ KCl at $100 \,\mathrm{mV_{rms}}$.

	$R_{\text{bulk}} [\mathbf{k}\Omega]$	$R_{\rm wires} \left[\Omega\right]$	$C_1 [\mathrm{nF}]$	$C_2 [\mathrm{nF}]$	$\omega^*/2\pi$ [kHz]	$\omega_D/2\pi$ [MHz]
A50	3.5	7.6	26	0.28	11.2	1.0
A75	5.2	7.6	26	0.19	7.5	1.0
A100	6.8	7.6	26	0.15	5.6	1.0

Table 7.4: Roughly estimated values of components in the equivalent circuits for channels containing electrodes of varying geometries. They have been estimated on the basis of the considerations presented in Chapter 3. The electrolyte is a 0.1mM KCl solution, and the electrode material is platinum.

These calculations of the components in the simple equivalent circuit corresponds qualitatively to the observed impedance spectra of Fig. 7.7. The frequency ω_D was apparently unchanged and the bulk resistance scaled corresponding to p, which has the values 39, 26 and 20 for A50, A75 and A100, respectively. It is more difficult to estimate ω^* from the measured curves, since the full spectrum is not covered. In Table 7.4 the values of the electrical equivalent components are roughly estimated on basis of Table 7.3, Eqs. (7.4) and (7.5), and the *RC* frequencies are noted. Clearly, the measured bulk resistances are approximately half of the estimated value, however, the scaling fits. Regarding the frequencies, it may be concluded that the estimated values agree within an order of magnitude.

It should be noted that the equivalent model also predicts a nearly invariant phase spectrum, though the slight change of the estimated ω^* also reflects in the spectrum.

Variation of the electrolyte concentration

For the chip type A50 with translation period $50 \,\mu\text{m}$, impedance spectra were obtained for the two electrolyte types in different solutions.

In Fig. 7.8 four spectra are shown for the channel containing electrolytic borax solutions of $0.1 \,\mathrm{mM}$, $0.5 \,\mathrm{mM}$, $1 \,\mathrm{mM}$ and $10 \,\mathrm{mM}$ concentrations. It should be noted that the full



Figure 7.8: Impedance spectra measured on chip A50 at $100 \,\mathrm{mV_{rms}}$ for various borax solutions.



Figure 7.9: Impedance spectra measured on chip A50 at $100 \,\mathrm{mV_{rms}}$ for various KCl solutions.

spectrum was not investigated for the electrolytic concentration of 10 mM, since the electrode damaging occured at higher frequencies when the concentration was increased. This observation is supported by the investigations of Studer *et al.*. Fig. 7.9 correspondingly shows impedance spectra obtained for the channel containing KCl solutions of 0.1 mM, 0.2 mM, 0.3 mM and 1 mM concentrations.

It was observed how an increased concentration of the electrolyte resulted in generally lowered absolute impedance spectra. Also the characteristic frequencies seemed to change with altered electrolytic concentration. The absolute impedance tends towards the same value for all concentrations in the high frequency limit. From the phase spectrum it is clearly seen how the characteristic frequencies were shifted upwards for increasing electrolyte concentration.

In Fig. 8.10 the impedance spectra of the two kinds of electrolytes are compared for the concentrations 0.1 mM, 1 mM. The spectra for each of the electrolytes differed slightly. A small difference was observed between the 0.1 mM solutions and the phases were shifted slightly.


Figure 7.10: Impedance spectra measured on chip A50 at $100 \,\mathrm{mV_{rms}}$ for various KCl and borax solutions. The spectra are equivalent with spectra previously shown in Figs. 7.8 and 7.9. This plot emphasize the impedance difference between borax and KCl electrolytes of the same concentrations.

	$R_{\text{bulk}} [\mathrm{k}\Omega]$	$R_{\rm wires} \left[\Omega\right]$	$C_1 [\mathrm{nF}]$	C_2 [nF]	$\omega^*/2\pi$ [kHz]	$\omega_D/2\pi$ [MHz]
0.1 mM	3.5	7.6	26	0.28	11	1.0
0.3 mM	1.2	7.6	45	0.28	18	2.9
1 mM	0.37	7.6	80	0.28	34	9.6

Table 7.5: Rough estimates of the components in the equivalent circuits for channels containing various aqueous KCl solutions. The channel geometry is A50, and the electrode material is platinum.

Estimates of the components in the corresponding equivalent diagram relates for different electrolytic concentrations as outlined in Table 7.5. Comparing these values with the obtained spectra it is seen that the scaling of the bulk resistance fits rather well, however, the estimated value is still approximately a factor of two larger. A rather large shift of the estimated characteristic frequencies is also apparent, which corresponds to the observed frequency shifts.

In the equivalent model, the scaling of the bulk resistance corresponds directly to the relation between the electrolytic conductivities. This is also seen in the comparison of the spectra obtained for borax and KCl, where similar concentrations have different conductivities.

Variation of the oscillation voltage

Impedance spectra have been measured for various oscillation voltages on chip A50 containing 0.1 mM KCl solution.

In Figs. 7.11 and 7.12 impedance spectra are shown for five different oscillation voltages, 10 mV_{rms} , 50 mV_{rms} , 100 mV_{rms} , 500 mV_{rms} and 1 V_{rms} . They are measured for both kinds of electrolytes in two different solutions, 0.1 mM and 1 mM. For the low concentration electrolyte, no significant changes were observed for neither the absolute impedance nor the phase. The spectra obtained for higher concentrations showed a small difference in



Figure 7.11: Impedance spectra measured on chip A50 at $100 \text{ mV}_{\text{rms}}$. The voltage has been varied between $10 \text{ mV}_{\text{rms}}$ and 1 V_{rms} for two different KCl solutions. Graphs a) and b) are obtained for 0.1 mM KCl, and graphs c) and d) are measured for 1 mM KCl.

the low frequency regime. The difference seemed more pronounced for the borax solution spectra. It was observed that voltages higher than 100 mV caused the absolute impedance to decrease for low frequencies and the phase to become less negative. This development seemed to become more explicit for increasing voltages.

It does not make sense to discuss the equivalent diagram model for different voltages, since the modelled components are ideal and do not change with neither voltage nor frequency. A possible explanation may instead be found in the electro chemistry. As mentioned in Section 3.1 the impedance does not in the real system tend towards infinity in the DC limit. Electrode reactions occur and allow a small Faradaic current to flow. The resistance against this current is very high, but changes with the applied voltage difference [4]. The resistance against current flow is smaller when the applied voltage difference become large. This could explain the lowered absolute impedance value in the low frequency regime. Regarding the difference between high and low concentrations, this may be explained on the basis of the shift in characteristic frequency. The difference between high and low voltage curves might occur for even lower frequencies when the concentration is decreased, and since the swept frequency range is the same for both



Figure 7.12: Impedance spectra measured on chip A50 at $100 \text{ mV}_{\text{rms}}$. The voltage has been varied between $10 \text{ mV}_{\text{rms}}$ and 1 V_{rms} for two different borax solutions. Graphs a) and b) are obtained for 0.1 mM borax, and graphs c) and d) are measured for 1 mM borax.

concentrations this effect might not be seen.

7.2.3 Evaluation of the equivalent diagram

In Fig. 7.13 an absolute impedance spectrum is curve fitted in accordance with the previously presented and utilized equivalent diagram. The plotted spectrum is obtained on chip A50 containing 0.1 mM KCl solution and measured at an oscillation voltage of 10 mV_{rms} .

The curve fit of the measured spectrum is rather good, and the estimated values corresponds within an order of magnitude to the very roughly estimated equivalent component values, see Table 7.6. This indicates that the effects giving rise to the shape of the absolute impedance curve are understood, though it may be argued that the roughly estimated value of C_1 is much too low.

However, a further investigation of the equivalent circuit might indicate that the system is not yet fully understood. In Fig. 7.14 the real and imaginary part of the measured impedance spectra have been plotted. The curve fit in Fig. 7.14a is the best possible fit for the outlined equivalent circuit. It is clearly seen that especially the real part is fitted poorly at low frequencies. The measured curve diverges while the model shows a constant



Figure 7.13: Impedance spectrum obtained for chip A50 containing 0.1 mM KCl at 10 mV. The absolute impedance spectrum $|Z(\omega)|$ is curve fitted according to Eq. (7.3c) neglecting R_{wires} . The results are listed in Table 7.6.

	$R_{\text{bulk}} [\mathrm{k}\Omega]$	$R_{\rm wires} \left[\Omega\right]$	$C_1 [\mathrm{nF}]$	$C_2 [\mathrm{nF}]$	$\omega^*/2\pi$ [kHz]	$\omega_D/2\pi$ [MHz]
Estimate	3.5	7.6	26	0.28	11	1.0
Curve fit	1604	-	254	0.35	4.0	1.8

Table 7.6: Comparison of the values found by a curve fit of the absolute impedance spectrum measured on an A50 geometry containing 0.1 mM KCl solution and the roughly estimated component values.



Figure 7.14: Imaginary and real parts of the impedance spectrum obtained for a A50 geometry containing 0.1 mM KCl at 10 mV. a) The curves are fitted according to the simple equivalent diagram approximation, Eq. (7.3c). b) The curves are fitted to the same equivalent diagram approximation, but in this case a 10°C phase shift has been included.



Figure 7.15: Measurements of an equivalent circuit corresponding to Fig. 7.5 build of linear electronic components with the values $R_{\text{bulk}} = 1.47 \text{ k}\Omega$, $C_1 = 220 \text{ nF}$, $C_2 = 0.33 \text{ nF}$ and $R_{\text{wires}} = 0\Omega$. a) Measured at $10 \text{ mV}_{\text{rms}}$, and b) measured at $1V_{\text{rms}}$. The curves are fitted perfectly, thus, the measurements obtained by the Impedance Analyzer are reliably.

value in the DC limit.

It was attempted to shift the phase in order to optimize the curve fit. If an uncorrected phase shift had been included in the measured spectra, the diverging imaginary part of the spectrum would have affected the real part as well. The fit showed in Fig. 7.14b includes a phase shift of approximately 10 degrees, and the result is not much better. In this case, the imaginary measurement curve is fitted rather poorly. Additionally, it seems unlikely that such a large phase shift should have been included in the measurements since compensation measurements were made.

An electrical circuit was constructed to check the reliability of the Impedance Analyzer¹. Components of corresponding sizes were chosen; $R_{\text{bulk}} = 1.47 \,\text{k}\Omega$, $C_1 = 220 \,\text{nF}$ and $C_2 = 0.33 \,\text{nF}$. Their spectrum was measured for two oscillation voltages, $10 \,\text{mV}_{\text{rms}}$ and $1 \,\text{V}_{\text{rms}}$, and the real and imaginary parts are plotted in Fig. 7.15. These curves are fitted perfectly, thus, the diverging real part of the results presented in this chapter must be due to the characteristics of the physical system.

The components of the equivalent diagram are approximated by ideal electrical components, which are independent of frequency. This is clearly a rough simplification of the physical system, since the electrolyte consists of movable ions responding to the applied frequency. This affects both the bulk resistance and the capacitances of the system, which are all frequency dependent. Considering Fig. 7.13, this frequency dependence is suggested by the level in the middle, which is interpreted as the bulk resistance of the system. Contrary to the fitted curve, which is horizontal, the measured spectrum is slightly inclined at this level indicating a frequency dependence. Nonlinearities of the system become relevant in the high voltage regime, where the Debye–Hückel approximation no longer applies. The spectra measured at 10 mV_{rms} should be within the Debye–Hückel limit ($\ll 25$ mV).

¹According to the manual, the uncertainty of measurements obtained with the Impedance Analyzer are generally 3.0% at low frequencies (100 Hz) and 6.3% at high frequencies (10 MHz).



Figure 7.16: Imaginary and real parts of the impedance spectrum obtained on micropumps containing air at 10 mV. The curves are fitted according to the simple equivalent diagram approximation, Eq. (7.3c). a) Obtained on chip A50. b) Measured on chip A75. c) Obtained on chip A100.

However, the value is close to the upper limit with an amplitude of 14 mV.

Returning to the spectra measured for channels containing air, their real and imaginary parts have been presented in Fig. 7.16. The shape of the A50 spectra corresponds nearly perfect with an equivalent circuit consisting of a parallel coupled resistor $R = 7.7 \,\mathrm{k\Omega}$ and capacitor $C = 24 \,\mathrm{pF}$. The system is without liquid that in the previous examples gave rise to the extra large capacitance in the model because of the Debye layer. In this case the capacitance is mainly between adjacent electrodes, where the glass bottom is the medium. However, the spectra of the other geometries are more difficult to explain. A divergence was observed for both the imaginary and real part, and it became more pronounced for increasing distance between the electrodes.

As a last note, the electrode resistance has been measured on the meander shaped electrode test chip, and the absolute impedance is shown in Fig. 7.17. From the geometry of the electrode and the resistivity of platinum, the total resistance is estimated to approximately 380Ω and the measurement shows 415Ω . In the high frequency end a capacitive effect of the glass substrates is seen.



Figure 7.17: Electrode resistance measured on the fabricated meander shaped electrode. The resistance is measured to be 415 Ω , while a resistance of 380 Ω is expected. A capacitive effect is seen in the high frequency regime.

7.2.4 Long term effects?

During the measurement phase, one chip was used for various measurements, and the same impedance measurement was performed under exact same circumstances in connection with different experiments. In Fig. 7.18 four measurements have been performed on chip A50 containing 0.1 mM KCl solution at 100 mV. From A to D two weeks with measurements have passed. For the absolute impedance spectra A-C the exact same electrolytic solution has been used, while D was measured for a new solution mixture. This solution had a slightly higher concentration than the previous. This last concentration was measured to $\sigma = 1.44 \times 10^{-3} \,\text{S/m}$ at 23.1°C. Since the impedance generally decreased with time, it might be a sign of slow corrosion of the electrodes during use.



Figure 7.18: Impedance spectra obtained on chip A50 containing 0.1 mM KCl at 100 mV. The spectra are measured at different times during the weeks of measurements, starting with A and ending with D. The tendency is a decreasing impedance, possibly due to electrode wearing.

7.3 Summary

Impedance spectra were obtained for various micropumps and an equivalent diagram for the electrical circuit has been presented. In the context of this equivalent diagram, the absolute impedance spectrum is rather well understood and may be used for explaining some of the effects in the system. While varying both the translation periods as well as the electrolytic concentrations, series of impedance spectra were constructed. Again, the trends of the measured curves are explainable based on the equivalent diagram, and the roughly estimated parameter values fits within an order of magnitude.

Variations in the applied voltage resulted in deviating curves in the low frequency regime. This could possibly be due to electrokinetic effects at the electrodes.

A more thorough inspection of the equivalent diagram, shows that the diagram does not sufficiently describe the physical system. Especially for low frequencies, deviations from the theory are observed. This might be result of system nonlinearities that are introduced as a consequence of the rather high external oscillation voltages. It should also be noted that the estimated components are not ideal but frequency dependent.

Chapter 8

Flow measurements

In the last part of the measurement phase, the ability to create flow velocity was tested on the fabricated microchips. Fluorescent beads were injected into the detection area of the microchannel, and utilizing the setup described in Section 6.2, a series of pictures were acquired and used for determining the velocity of the beads. Flow generation was observed for three different microchips having different electrode translation periods. Primarily, flow velocity measurements were obtained over a range of frequencies with unaltered voltage amplitude. Velocity curves were then measured for the two electrolytes borax and KCl, introduced in Section 7.1, and KCl was applied in various concentrations. Additionally, curves were measured for three different voltages of $1 V_{\rm rms}$ to $2 V_{\rm rms}$, i.e., only in the nonlinear high voltage regime. The results of the velocity measurements are presented in Section 8.2, where also a comparison with the theoretical velocities presented in Chapter 3 is considered. The following section contains a short description of the measured hydraulic resistance in the channels.

8.1 Hydraulic resistance

With the setup for determining hydraulic resistance, Section 6.2, a number of the fabricated chips were tested. This measurement was performed before the electrical characterization, and during this experiment the leaking microchips were located and discarded. The leaking chips showed a significant lowered hydraulic resistance.

In Fig. 8.1 the measurement data for chip A100 is shown. The plot is the output of the Matlab program shown in Appendix E and the hydraulic resistance was measured to be $1.25 \times 10^{13} \,\mathrm{Pa}\,\mathrm{s/m^3}$ for this chip. Eight chips were tested and the channels showed the same resistances within 10% deviation.

From Eq. (2.21) the hydraulic resistance of the channels can on the basis of the channel dimensions be estimated to $1.37 \times 10^{13} \text{ Pa s/m}^3$, using the parameters listed in Table 8.1. The tubes connecting the channel with the pressure sensors additionally have a total resistance of approximately $9.1 \times 10^{10} \text{ Pa s/m}^3$. Thus, the theoretical resistance is $R_{\text{hyd}} \sim 1.38 \times 10^{13} \text{ Pa s/m}^3$ for this setup.



Figure 8.1: Hydraulic resistance measured for chip A100. Six pressure differences were applied across the microfluidic channel and the corresponding flow rates were measured. These data points are marked with crosses. A linear fit was made, indicated by a line, and the hydraulic resistance was determined from the slope. For this measurement it was $R_{\rm hyd} = 1.25 \times 10^{13} \,\mathrm{Pa} \,\mathrm{s/m^2}.$

8.2 Flow velocity

8.2.1 Flow measurement procedure

Preparation of the chip for flow measurements was much alike the procedure employed during the impedance measurements, described in Section 7.2. The electrolyte was carefully injected into the channel and tubing system, after which the three valves to in- and outlets were closed. After approximately 20 min, an impedance spectrum was measured using the Impedance Analyzer. After the pump measurements were finished, another impedance spectrum was obtained to verify that no electrode damaging had occurred during the experiments.

Before initiating the flow measurements, the liquid circuit was placed under a microscope and connected with the Lock-In Amplifier circuit. Beads were then injected into the



Figure 8.2: Micrographs obtained during flow generation on chip A50 containing 0.1 mM KCl solution. The applied voltage was 1.5 V and the frequency was 1.3 kHz. The beads have a velocity of approximately $122 \,\mu\text{m}$, and the arrows indicate the position of a single bead at three different times corresponding to three different sampling points. channel through the narrow bead inlet, which was subsequently closed. In order to minimize undesired spreading of the beads due to pressure differences in the tubing circuit, all minor valves were kept closed, while opening the outer pump loop by turning the four-way valve. Hereafter, the two minor valves were opened and the measurements were started. During the velocity measurements, the sampling rate of the attached camera was adjusted according to the bead velocities. An example of the pictures acquired during fluid flow is shown in Fig. 8.2. It should be noted that the determined velocities are averaged over a distance of 200 μ m.

It was first attempted to use beads with a diameter of 4 µm for the flow observations, however, with a mass density of $\rho = 1.05 \times 10^3 \,\text{kg/m}^3$ these beads fell rather fast through the fluid-filled channel and settled on the bottom. Balancing the gravitation force with the Stokes drag force, the steady state velocity of the beads is given as $v = \Delta \rho_{\text{mass}} (4/3)\pi r^3 g/(6\pi\eta r) = 2 \,\Delta \rho g \, r^2/(9 \,\eta)$, where $\Delta \rho$ is the density difference between the electrolyte of viscosity $\eta = 10^{-3} \,\text{Pa/s}$ and the beads of radius r. The large beads with $r = 2 \,\mu\text{m}$ approximately passed half the channel height $H/2 = 16 \,\mu\text{m}$ within 37 s. Consequently, 1 µm beads with $r = 0.5 \,\mu\text{m}$ were used for flow detection, since they only fell half a channel height in 9.8 min, and mostly seemed easier to keep suspended in the aqueous solution.

It should be noted that a single velocity series obtained over a range of frequencies was in general measured without shutting the pumploop or touching the valves. However, this was not always possible, and for some of the series a change of electrolyte or refilling of beads is seen as a slight discontinuity in the row of measurement points. Furthermore, during the first measurements the lowest frequencies were not included in the measurement series in order to avoid electrode damaging.

8.2.2 Results of flow measurements

Based on the article of Olesen *et al.*, summarized in Section 3.2, theoretical values of the flow velocities may be estimated for a 0.1 mM KCl electrolyte. The characteristic velocity of the system is estimated from $u_0 = \epsilon V_0^2 / \eta l_0 (1 + \delta)$, where V_0 is the externally applied voltage, l_0 is the characteristic length of the system and δ is the relation between the capacitances of the Debye layer and the Stern layer. From the plot in Fig. 3.8a showing the flow velocity as a function of frequency in the Debye–Hückel limit, the maximal flow velocity is determined as $0.004 u_0$. This corresponds to the maximum velocity at the bottom line of Fig. 3.8b, where the applied voltage is low. In the present experiments, the external voltages were 1-2 V_{rms} corresponding to dimensionless values of $\tilde{V}_0 = 55$ -110. From the contour plot the corresponding maximal velocities are then estimated as $0.00075 u_0 - 0.0016 u_0$. The resonance frequency in the high voltage regime is given by $\omega^* = R_0 C_s = \delta (\sigma \lambda_D)/(l_0 \epsilon)$.

Some of the values used in the calculation of flow velocities and resonance frequencies are listed in Table 8.1. The amplitude V_0 of the applied signal is calculated from the root mean square value as $V_0 = \sqrt{2} V_{\rm rms}$. Since the electrolytes are in a aqueous solutions, the permittivity ϵ and viscosity η of water are used. The characteristic length of the system is given by the width of the narrowest electrode, thus, it differs for the three translation

Debye length	$\lambda_{\rm D} = 30{\rm nm}$
Conductance (0.1mM KCl)	$\sigma = 1.43\mathrm{mS/m}$
Characteristic length A50	$l_0 = 4.2 \mu\mathrm{m}$
Characteristic length A75	$l_0 = 6.3 \mu\mathrm{m}$
Characteristic length A100	$l_0 = 8.4 \mu\mathrm{m}$
Total channel length	$L = 40.8 \mathrm{mm}$
Channel covered with electrodes	$L_1 = 16 \mathrm{mm}$
Channel height	$H = 33.6 \mu\mathrm{m}$
Channel width	$w = 967 \mu\mathrm{m}$
Viscosity of electrolyte (water)	$\eta = 10^{-3} \mathrm{Pa/s}$
Permittivity of electrolyte (water)	$\epsilon = 80\epsilon_0$

Table 8.1: Summary of values necessary for the calculation of the theoretical flow velocities listed in Tables 8.2 and 8.3.

	$1\mathrm{V_{rms}}$	$1.5\mathrm{V_{rms}}$	$2\mathrm{V_{rms}}$	
	$v_0 \; [\mu m/s]$	$v_0 \; [\mu m/s]$	$v_0 \; [\mu m/s]$	$\omega^* [{\rm kHz}]$
A50	144	264	414	1.4
A75	96	176	276	0.96
A100	72	132	207	0.72

Table 8.2: Theoretically estimated flow velocities v_0 at the resonance frequency ω^* for the micropumps A50, A75 and A100. The velocities are calculated for the voltages $1 V_{\rm rms}$, $1.5 V_{\rm rms}$ and $2 V_{\rm rms}$ when $\delta = 0.1$

	$1\mathrm{V_{rms}}$	$1.5\mathrm{V_{rms}}$	$2\mathrm{V_{rms}}$	
	$v_0 \; [\mu m/s]$	$v_0 \; [\mu m/s]$	$v_0 \; [\mu m/s]$	$\omega^* [\mathrm{kHz}]$
A50	151	276	434	0.72
A75	101	184	290	0.48
A100	76	138	217	0.36

Table 8.3: Theoretically estimated flow velocities v_0 at the resonance frequency ω^* for the micropumps A50, A75 and A100. The velocities are calculated for the voltages $1 V_{\rm rms}$, $1.5 V_{\rm rms}$ and $2 V_{\rm rms}$ when $\delta = 0.05$

periods. For high voltages, the Debye layer capacitance become very large and the double layer capacitance is dominated by the Stern layer. The capacitance ratio $\delta = \epsilon / \lambda_{\rm D} C_s$ is rather small (≤ 1) in this regime. The exact value is difficult to determine, which is why two different values have been used for the estimated velocities, 0.1 and 0.05.

The theoretical velocities estimated on the basis of the article by Olesen are slip velocities right above the electrodes. For comparison, the measured velocities have to be scaled in relation to the dimensions of the channel and the varying flow profiles. The generated flow in the channel section containing electrodes has the form of a couette flow, Section 2.3. In addition, a resulting backpressure gives rise to a parabolic shaped velocity profile in the reverse direction. For the channel section without electrodes, where the

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bead velocities were detected, the flow is entirely pressure driven having a parabolic profile. The hydraulic resistance of the channel section containing electrodes is denoted R_1 and the hydraulic resistance of the section without electrodes is R_2 . The pressure driven flow rates of the two channel sections may be written as

$$Q_1 = -\Delta p/R_1, \qquad Q_2 = \Delta p/R_2.$$
 (8.1)

The flow rate generated by the Couette flow is denoted Q_0 , and the total flow rate through the entire channel must then be given by

$$Q = Q_2 = Q_1 + Q_0 = Q_0 \frac{R_1}{R_1 + R_2},$$
(8.2)

utilizing Eq. (8.1). If the slip velocity of the Couette flow is u_0 , the flow rate, Eq. (2.15), is $Q_0 = Hwu_0/2$, where H is the channel height and w is the channel width.

The resistance of the outer pump loop is neglected in this calculation, since the theoretical resistance of the tubing is 1000 times less than the channel resistance. Consequently, it is assumed that there is no pressure difference across the channel in- and outlets. The pumping velocity is detected from beads with maximum velocity in a Poiseuille flow profile. This corresponds to a velocity of, Eq. (2.17),

$$v_x(H/2) = v_{x,\max} = \frac{\Delta p H^2}{8\eta L_2},$$
(8.3)

assuming two infinitely wide parallel plates, and the length L_2 of the channel section without electrodes. The pressure difference is given by Eqs. (8.1) and (8.2), leading to the following scaling factor between the detected velocity $v_{x,\max}$ and the slip velocity at the electrodes U:

$$v_{x,\max} = Q_0 \frac{R_1 R_2}{R_1 + R_2} \frac{w H^3}{16\eta L_2} U.$$
(8.4)

The resistances of the two channel sections, R_1 and R_2 , are given by the expression of Eq. (2.18) as $H^3w/12\eta L$. Inserting this into Eq. (8.4), leads to the following simple geometrical relation:

$$U = \frac{3}{4} \frac{(L_1 + L_2)}{L_1} v_{x,\max} = 3.4 v_{x,\max}$$
(8.5)

Here L_1 is the length of the channel containing electrodes, and L_2 is length of the remaining channel.

The theoretically estimated slip velocities are divided by 3.4 and the resulting expected velocities v_0 are listed in Tables 8.2 and 8.3 for the two different values of δ .

Variation of the translation period

Flow generation was observed on three different chips having dissimilar electrode translation periods. Velocity measurements are shown in Figs. 8.3 and 8.4 for chip A50, A75 and A100, with translation periods $50 \,\mu\text{m}$, $75 \,\mu\text{m}$ and $100 \,\mu\text{m}$, respectively. The flow was generated with 0.1 mM KCl in the channel at two different voltages, $1 \,\text{V}_{\text{rms}}$ and $1.5 \,\text{V}_{\text{rms}}$.



Figure 8.3: Flow velocities generated on chip A50 and A75 having translation periods of 50 μ m and 75 μ m, respectively. The electrolyte was a 0.1 mM KCl solution and the applied external voltage was $1 V_{\rm rms}$.



Figure 8.4: Flow velocities generated on the chips A50, A75 and A100 having translation periods of $50 \,\mu\text{m}$, $75 \,\mu\text{m}$ and $100 \,\mu\text{m}$, respectively. The electrolyte was a $0.1 \,\text{mM}$ KCl solution and the applied external voltage was $1.5 \,V_{\rm rms}$.

Moving from high frequencies towards the low frequency area, it was generally observed that flow generation began around 10 to 20 kHz. The velocity was seen to increase with decreasing frequency, and it did not seem possible to convincingly reach a resonance peak without risking electrode damage. It was attempted to decrease the frequency further for the micropump A100, but the electrodes were damaged during the measurements, which were continued down to 0.5 kHz. Overall, comparison of the measured series clearly show that the velocity increased with decreasing translation period.

If the velocities are compared with the theoretical values of Tables 8.2 and 8.3 it is

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	A50	A75	A100
	$[\mu m/s]$	$[\mu m/s]$	$[\mu m/s]$
Theory	265	149	86
Measurement	135	63	28

Table 8.4: Theoretically estimated flow velocities v_0 at 1.1 kHz for the micropumps A50, A75 and A100. The velocities are calculated for the voltage $1.5 V_{\rm rms}$ when $\delta = 0.05$, and compared with the observed values plotted in Fig. 8.4.

generally seen that the measured velocities are very low. A resonance peak is indicated, and it fits with the value calculated for A75 when δ is 0.1. However, for this value of δ , a resonance peak should have been observed at 1.4 kHz for the translation period of A50. Only one velocity measurement point, in Fig. 8.3 at 0.7 kHz, indicates that a resonance peak was found. Due to the measurement uncertainties of the velocity determination, discussed in a later subsection, the existence of a resonance peak at this point cannot be fully ascertained.

Assuming that no resonance was present, the measurements may indicate a low δ around 0.5. Here it should be stressed that the factor δ strongly influences the resonance frequency and is less important with regard to the velocity in this high voltage regime. This is clearly seen in the expressions for ω^* and u_0 outlined previously. If the flow velocity peaks at the frequencies listed in Table 8.3, Fig. 3.8b may be used for an estimate of the expected velocities at 1.1 kHz for each of the three micropmups. This has been done for the measurements at $1.5 V_{\rm rms}$. The dimensionless $\tilde{\omega}$ corresponding to 1.1 kHz for each of the translation periods has been calculated and the corresponding dimensionless velocity determined from the theoretical velocity contour plot. The difference between the calculated resonance frequencies are in this way compensated so that the velocities of the same frequency may be compared. In Table 8.4 the expected velocities at 1.1 kHz are compared with the measured.

However, the flow velocity estimates are too high. Qualitatively, the determined values relate as expected, with the difference between series A50 and A75 being significantly larger than the difference of series A100 and A75.

Concentration variation

On chip A50, the effect of changes in the electrolytic concentration was investigated through a series of measurements. More specifically, KCl solutions of three different concentrations, 0.1 mM, 0.2 mM and 0.3 mM, were employed to generate flow at two different voltages, $1 V_{\rm rms}$ and $1.5 V_{\rm rms}$. The measurement series are shown in Figs. 8.5 and 8.6.

The flow velocity series obtained at $1 V_{\rm rms}$ for an electrolyte concentration of $0.2 \,{\rm mM}$, Fig. 8.5, had a rather unstable course. This was probably due to the uncertainties related to the velocity determination method. However, there was apparently no difference between the curves measured for the two concentrations $0.1 \,{\rm mM}$ and $0.2 \,{\rm mM}$.

For the series measured at $1.5 V_{\rm rms}$, Fig. 8.6, more reliable tendencies were observed. Generally, the fluid flow velocity decreased as the electrolytic concentration was increased.



Figure 8.5: Flow velocities measured on chip A50 at $1 V_{\rm rms}$. The applied electrolytes were KCl solutions with the concentrations 0.1 mM and 0.2 mM.



Figure 8.6: Flow velocities measured on chip A50 at $1 V_{\rm rms}$. The applied electrolytes were KCl solutions with the concentrations $0.1 \,\mathrm{mM}$, $0.2 \,\mathrm{mM}$ and $0.3 \,\mathrm{mM}$.

This concentration dependency was most obvious in the low frequency regime, while the series of 0.1 mM and 0.2 mM displayed almost identical flow velocities at higher frequencies. It was observed that the difference between the series at the lowest measured frequency was nearly the same $\sim 30 \mu m/s$.

Considering the previously discussed theoretical flow velocities, the observed tendency, characterized by a decreasing velocity as the concentration is increased, does not concord with the expected results. The absolute velocity should not be affected by the changed concentration, only δ might change. Since δ is small the velocity is proportional to $1/(1+\delta)$, this change is not assumed to have an impact on the flow. Furthermore, the resonance peak is not supposed to shift towards lower frequencies. The Debye length scales with the

square root of the reciprocal concentration. In the expression of the resonance frequency, the concentration is multiplied with the Debye length and, consequently, the velocity peak should shift upwards in the frequency spectrum for increasing concentration.

It should be noted that the tendency of an inverse relation between flow velocity and concentration, is confirmed by the observations of Studer *et al.* [3].

Variation of the oscillation voltage

The externally applied voltage was varied, whereby velocity series of $1 V_{\rm rms}$, $1.5 V_{\rm rms}$ and $2 V_{\rm rms}$ were obtained. The series were measured at two different chips, A50 and A75, and for the electrolytes 0.1 mM KCl and 0.1 mM borax. The series are plotted in Fig. 8.7, Figs. 8.8 and 8.9 . In Fig. 8.10 the series of Figs. 8.8 and 8.9 are plotted together for comparison of the two electrolytes.



Figure 8.7: Flow velocities measured on chip A50 for a 0.1 mM KCl solution. The applied voltages were $1 V_{\rm rms}$ and $1.5 V_{\rm rms}$. The three different series obtained at $1.5 V_{\rm rms}$ were obtained at different days of measuring.

It should be noted that the two equal series of Fig. 8.7 (A1.5V and B1.5V) were obtained with a few days interval in order to check the reproducibility of the flow velocities in the system. The low frequency series (C1.5V) was obtained in the last part of the measurement phase.

For both electrode translation periods, A50 and A75, exposed to 0.1 mM KCl it was observed that the velocity generally increased with increasing voltage, Figs. 8.7 and 8.8 . A very large velocity increase of approximately $110 \,\mu$ m/s was seen at 1.1 kHz on A50 between the series of $1 \, V_{\rm rms}$ and $1.5 \, V_{\rm rms}$. The velocity increase was less on A75, and for the series of $1.5 \, V_{\rm rms}$ and $2 \, V_{\rm rms}$ the difference became very small for frequencies over 1.7 kHz. Furthermore, these latter two series did not seem to show a steadily increasing flow for decreasing frequencies. They have a nearly unchanged flow rate over the frequencies 3-1.7 kHz, after which they increase abruptly.



Figure 8.8: Flow velocities measured on chip A75 for a 0.1 mM KCl solution. The applied voltages were $1 V_{\rm rms}$, $1.5 V_{\rm rms}$ and $2 V_{\rm rms}$.

Returning to the theoretically estimated values of Table 8.3, they predict a difference between the series obtained on A50 of about 125 μ m/s, which is not far from the measured difference. However, the absolute value has been overestimated as previously mentioned. Note that the voltage series may be directly compared, since the resonance frequency should not be affected by a change in the applied voltage. The series measured on chip A50 containing 0.1 mM KCl may be directly compared with the results obtained by Studer *et al.* [3]. In this article, the same electrode dimensions and electrolyte have been applied, only the channel geometry is different, resulting in another directly detected fluid velocity. In this work, resonance peaks were observed at approximately 1kHz, and the detected maximum flow velocities were 10 μ m/s at 1 V_{rms} and 65 μ m/s at 1.5 V_{rms}. Multiplying these velocities with a factor of two, the observed velocities at 1.1 kHz of Fig. 8.7 is obtained. Regarding the series measured on A75, they qualitative show the expected tendency. For 1.1 kHz, the largest velocity increase is seen from 1.5 V_{rms} to 2 V_{rms} compared to the increase from 1 V_{rms} to 1.5 V_{rms}.

In Fig. 8.9, three series are shown that were measured on chip A75 containing a borax solution. As before, an increase in the flow velocity occured when the voltage was increased and the frequency decreased. However, for the series measured at $2 V_{\rm rms}$ a peak was seen at approximately 2 kHz, after which the velocity decreased as the frequency was further decreased. The velocity reached zero at approximately 1.4 kHz and for lower frequencies it became negative, i.e., the flow generation was reversed. A resonance peak was additionally observed at $1.5 V_{\rm rms}$, but this occurred for a slightly lower frequency, 1.3 kHz.

In Fig. 8.10 the series of borax and KCl at the same concentration measured on the same chip are compared for the three voltages. In general, the KCl series have a higher velocity compared to the borax series obtained at a corresponding voltage. The two series at $1.5 V_{\rm rms}$ and $2 V_{\rm rms}$ apparently have the same course for high frequencies. They follow each other from high towards lower frequencies until the borax series peaks, after which



Figure 8.9: Flow velocities measured on chip A75 for a 0.1 mM borax solution. The applied voltages were $1 V_{\rm rms}$, $1.5 V_{\rm rms}$ and $2 V_{\rm rms}$.



Figure 8.10: Comparison of the flow velocities measured on chip A75 for 0.1 mM borax or KCl solutions. The applied voltages were $1 V_{\rm rms}$, $1.5 V_{\rm rms}$ and $2 V_{\rm rms}$. The plotted series are equivalent with the series plotted in Figs. 8.8 and 8.9.

the KCl series increases abruptly and the borax series decreases.

The borax solutions have a higher conductivity compared to KCl at the same concentration. This could be the reason for the reduced velocity, since higher conductivity (or higher concentration) previously has been observed to lower the flow velocity.

Reverse pumping

In relation to the variation of concentration, it was attempted to measure a series on A50 at $1 V_{\rm rms}$ containing 0.3 mM KCl solution. At the starting frequency 2.5 kHz, the flow



Figure 8.11: Flow velocities measured on chip A50 for a 0.3 mM KCl solution as a function of voltage. The applied frequency was 2.5 kHz. Note that the velocity is negative or "reversed" below $1.2 V_{\rm rms}$.

generation was reversed. Instead, a series of varying voltage was obtained, since a series at $1.5 V_{\rm rms}$ had previously been obtained, which showed normal pumping at all frequencies. The measured voltage series is shown in Fig. 8.11.

Reverse pumping has been reported by Studer *et al.* [3], but not for this voltage and frequency regime. Instead, it was observed for voltages above $2 V_{\rm rms}$ and frequencies above 10 kHz. It should be noted that the maximum reverse pumping speed in this case is approximately 7 μ m.

Sources of error

In the flow experiments carried out during this project, the most important source of error was the flow determination process.

The flow velocity for specific values of applied voltage and electrolyte concentration was determined by counting the number of acquired frames, while following a bead over a range of 200 μ m. Since the frame capture rate was adjusted according to the bead velocity, the uncertainty on the number of frames over the distance was approximately equal for all measurements. It is estimated that this counting procedure introduces an error of approximately $\pm 6 \,\mu$ m on the flow velocity.

Moreover, the flow profile in the detection channel also introduces an error. It was difficult to locate the fastest particle representing the maximum velocity in the parabolic flow profile. The statistical uncertainty of determining the maximum speed also increased if only a few moving particles were present in the channel. This was sometimes the case, since flow generation could be hindered by bobbles in the system. Before these problems could be solved, many particles had already settled on the channel bottom. If it is assumed that the detected particles are located within the middle third of the channel height, the uncertainty due to the parabolic velocity profile is approximately 10% of the velocity, i.e.,

 $10\,\mu\text{m}$ for the fastest particles. When enough particles are present in the channel, this uncertainty is significantly less.

During the measurements, a few beads came in contact with the electrode array and settled on the metal. It is not known exactly how this influences the flow, yet, it was not desirable. In the worst case, there were beads settled on nearly every second electrode. It should however be noted that the bead diameter is only 1/4 of the narrowest electrode width. No difference was observed for the impedance spectrum and the velocity did not seem to be significantly affected.

Efforts were made to clean the channels, and a 0.2M HCl solution cleaned the glass surfaces, but nothing could remove the beads from the electrodes. Both soap (2% sds in pbs), and a 2% NaOH solution was attempted.

Comparison of flow velocity with theory

A last remark regarding the theoretically obtained velocities concerns the shape of the velocity curve as a function of frequency. An example of the curve obtained as a cross section in the nonlinear regime of Fig. 3.8b is shown in Fig. 8.12. The curve is plotted for 1.5 V and $\delta \sim 0.3$, and the flow velocity is down-scaled in order to compare the shapes. The measurement data were obtained on chip A50 containing 0.1mM KCl at 1.5 V_{rms} .



Figure 8.12: Theoretical velocity curve calculated for $\delta = 0.3$ and compared with experimental values obtained on chip A50 containing 0.1mM KCl at $1.5 V_{\rm rms}$.

8.3 Summary

During flow velocity measurements with flourescent beads, a pumping effect was detected on three different chips. Some of these measurements were compared with velocities obtained by Studer *et al.* Eventhough the same order of magnitude was observed, the directly detected velocities in the present system are twice the detected velocities by Studer.

Despite variations between some of the measured curves (10-15%), which were caused by a rather large uncertainty on the measurements, the overall reproducibility can in light of this uncertainty be characterized as satisfactory.

In general, it was difficult to detect a resonance frequency, yet indications of resonance frequencies were found for low voltage measurements. The reason is that the resonance frequencies of the systems investigated are located in a frequency regime were the risk of electrode damaging is high.

From a number of velocity measurement carried out for different electrode array translation periods, it was seen that the velocities changed correspondingly. This observation is supported by the theoretically calculated velocity differences. Varying the applied voltage resulted in curves, which also fit rather well with the theoretical values of the flow velocity calculated for the KCl solution, yet, the voltage curves of the Borax solution show reverse pumping and a frequency shifted resonance peak, which are not readily explainable.

Variations in the electrolyte concentration show a reduced velocity for higher concentration. This corresponds to the observations of Studer, but it differs from current theory, predicting an increased resonance peak, since this phenomenon was not observed during measurements.

Three functional chips were tested and all of them were able to generate a stable flow. The maximum velocities detected within these micropumps correspond to slip velocities above the electrode array of nearly ~ 0.5 mm/s.

Possible long term effects were observed. The impedance spectra for chip A50 containing 0.1 mM KCl decreased slowly during the measurement weeks. Correspondingly, the three flow measurements on chip A50 containing 0.1 mM KCl, were measured immediately after the impedance spectra were obtained, and these flow measurements showed a slightly lowered velocity each time, indicating a slow electrode corrosion.

Chapter 9

Evaluation and outlook

Many difficulties were encountered during processing of the micropumps, and the planned etching of in- and outlet holes never succeeded due to a permanent machine break-down. However, a complete process flow was developed for fabrication of micropumps with etched holes, and provided that a layer of amorphous silicon could be deposited on a Pyrex wafer, the pumps could be fabricated in this way.

The anticipated problems regarding short-circuiting between the electrode pairs in the array never became relevant. Thus, the electrode design could be improved by collecting all the wires leading from the contact pads to the electrode array into one broad wire. In this manner, there would be no bonding problems along the chip edge, where the wires in the present design may cause the chip to leak.

Generally, the bonding was satisfying, though the relatively thick electrode structures between the bonded substrates gave rise to micro cavities along the electrode edges. A smoothing of the surface would thus be desirable. Making the electrodes thinner would also be a solution, and to avoid a significantly increased electrode resistance materials like aluminum and gold, having a resistivity four times less than that of platinum, could be considered.

Regarding electrode wearing, it has been considered to protect the electrodes with a layer of oxide. For this purpose, materials such as aluminum and titanium were considered. Aluminum has a low resistivity, but the oxide of titanium is much more robust compared to the aluminum oxide. Consequently, it was considered to utilize a combination of metals. For instance a core of gold covered with titanium would be a solution with low resistance and a robust surface.

In the current wafer design, controlled electrode oxidation has been made possible and the first calibration tests have been performed. Because of problems during the first processing steps, the process flow was, however, never carried out. The perspective is to utilize naturally or controlled grown oxide in the system. Growing oxide of alternating thickness on the electrode array could be an alternative way of introducing a flow generating asymmetry in the system. It should additionally be considered whether this potential oxide layer is affected by usage of the pump.

Further investigations of the electrode geometry would be interesting. The lift-off

process has proved applicable for electrode spacings down to at least $3 \,\mu$ m. Hence, it would be possible to further down-scale the electrode translation period and presumably obtain increased flow velocities. According to theory, a decreased translation period should also lead to an increased resonance frequency of the system, and it might therefore be possible to detect the resonance without damaging the electrodes. Regarding geometry, it would additionally be rather easy with the present chip design to examine the confined geometry, where the electrode translation period becomes larger than the channel height.

An alternative process flow could be relevant in order to avoid the hole drilling in the present fabrication process. Fluorescent beads may be detected in a half transparent microchannel contained within a Pyrex substrate bonded to a silicon substrate. Either the process flow briefly discussed in Section 5.2 could be utilized, or a more simple solution based on Deep Reactive Ion Etch of channels and holes in a silicon wafer could be attempted. In the latter case, the processed silicon wafer should be oxidized and subsequently bonded to the Pyrex substrate containing electrodes. This would though introduce a possible capacitive coupling through the Si wafer.

Nevertheless, a fully transparent channel is still desirable. This opens for other detection methods such as optical tweezers, which could be employed to measure forces on single particles in the channel. Additionally, μ -PIV is a detection method, which could be utilized to measure the flow velocity profile. An aluminum bottom for the chip holder has been constructed, making it possible to have a microscope lens within a range of few millimeters from the chip surface, required for μ -PIV.

Regarding the pumploop, it might be preferable to have the entire loop build into the chip. It would then be easier to control that no bobbles remain in the system during pumping. However, it precludes the possibility for measuring the generated pressure difference across the electrode array.

The two electrode test chips were fabricated in order to study the basic hydrodynamics on the simplest possible systems, but due to time limitations they were never utilized. The analysis is still interesting and a comparison with the outlined analytically calculation would be relevant. However, the analytical solution might first be extended to two dimensions in order to obtain the right geometry. Investigations of the two electrode system may lead to a better understanding of the electrohydrodynamics and the failure of the simple equivalent diagram.

The IC electroosmotic pumping method may easily be down-scaled and integrated with a complete lab-on-a-chip system, and in addition, it is compatible with the microfabrication technology because of the simple design principles utilized. In fact, the pumping effect would actually increase as the device is down-scaled. Presently, the cleanroom processing techniques are the limiting factor, but owing to the continuous advances within this field, considerable improvements are to be expected with respect to the smallest dimensions that can be realised. As an example, E-beam lithography opens a possibility of fabricating very small electrode translation periods.

However, the pumping effect demonstrated in various experimental projects has so far been very weak, and the micropumps realised are perhaps better suited for mixing rather than pumping bulk volumes. The pumping effect has shown to be very dependent on conductivity, which from an application perspective is unfortunate. Even so, a high operating stability of the micropump can be expected, since electrode damaging is observed only for a combination of very low frequencies and high voltages. This bodes well for the suitability of this type of micropump in future applications. Taking the current level of performance into consideration, the AC electroosmotic micropump could presumably very soon be incorporated into common electronic systems with the purpose of efficient transistor cooling.

Chapter 10

Conclusion

During the project a rather large part of the time was spend designing and manufacturing the micropump devices. The fabrication caused unforeseen problems which ended up being very time consuming. The devices were though successfully completed and time was afterwards spend building the measurement setups before the actual tests could be performed. A minor part of the entire project time was spend performing analytical calculations.

The basics of hydrodynamics and electrohydrodynamics has been outlined, and the current theories about flow generation in an electrolyte above an asymmetric electrode array applied AC voltage has been summarized. An asymmetric electrolyte between parallel plates applied opposite time dependent voltages has been studied as a one dimensional analytical problem. For the time independent problem, a new Debye length was introduced and it was concluded that ions of different valences screen asymmetrically. Regarding the time dependent situation, it was concluded that the fast ions screen much of the wall potential until the Debye frequency is reached. For higher frequencies, the potential distribution between the walls becomes equal to that of a parallel plate capacitor. Furthermore, oscillations in the charge distribution were observed for intermediate frequencies.

Although the fabrication process proved extremely challenging and laborious, functional chips were successfully fabricated, and moreover, transparent channels with asymmetric electrode arrays were realized. The original plan of etching holes was abandoned due to a permanent machine breakdown, however, a complete process flow was developed, which will be directly applicable if the necessary machines are available. Caused by the inability of the hole etching step to be integrated in the process flow, holes were successfully drilled instead.

Impedance spectra were obtained for various micropumps and an equivalent diagram for the electrical circuit has been presented. In the context of this equivalent diagram, the absolute impedance spectrum is rather well understood and may be used for explaining some of the effects in the system. The trends of the measured curves are explainable based on the equivalent diagram, and the roughly estimated parameter values fits within an order of magnitude. A more thorough inspection of the equivalent diagram, shows that the diagram does not sufficiently describe the physical system. Especially for low frequencies, deviations from the theory are observed.

Three functional chips were tested and all of them were able to generate a stable flow. The maximum velocities detected within these micropumps correspond to slip velocities above the electrode array of nearly $\sim 0.5 \text{ mm/s}$. Some of the flow measurements were compared with velocities obtained by Studer *et al.* and the same order of magnitude was observed. The overall reproducibility can in light of the uncertainty on the measurements be characterized as satisfactory. In general, it was difficult to detect a resonance frequency, yet indications of resonance frequencies were found for low voltage measurements. The trends observed for varying electrode translation periods and varying applied voltage are supported by the theoretically calculated velocities, however, the observed velocities are generally much lower than expected. Variations in the electrolyte concentration show a reduced velocity for higher concentration. This corresponds to the observations of Studer, but it differs from current theory.

Possible long term effects were observed. The impedance spectra for chip A50 decreased slowly during the measurement weeks. Correspondingly, flow measurements on chip A50 showed a slightly lowered velocity.

Appendix A

Solution of analytical 1D problem

Mathematica programs used for solving and plotting the charge density deviations $\delta \rho_+$, $\delta \rho_-$ and the potential ϕ between two parallel plates with distance L and opposite harmonic oscillating potentials of amplitude V_0 . Section A.1 corresponds to an asymmetric electrolyte between the plates, and Section A.2 corresponds to an asymmetric electrolyte.

A.1 Time dependent symmetric solution

```
Clear["Global`*"];
Off[General::spell];
```

The six equations of the integration constants are contained in the following list named "eqs":

```
\begin{split} & eqs = \{-a1*(c3+c4)+c6 =: V0, -a1*(c3*e3+c4*e4)+c5*L+c6 =: -V0, \\ & (c2-c1)*a3+(c4-c3)*a4-c5*b1 =: 0, \\ & (c2*e2-c1*e1)*a3+(c4*e4-c3*e3)*a4-c5*b1 =: 0, \\ & -(c1-c2)*a3+(c3-c4)*a4+c5*b1 =: 0, \\ & -(c1*e1-c2*e2)*a3+(c3*e3-c4*e4)*a4+c5*b1 =: 0\}; \end{split}
```

The equations are solved, and the simplified solution is stored in "sol".

sol = Solve[eqs, {c1, c2, c3, c4, c5, c6}] // Flatten;

```
sol2 = Simplify[sol];
```

All the known constants (real and imaginary) used to reformulate the six equations are listed in "const".

 $\begin{aligned} & \text{const} = \left\{ \mathbf{a1} \rightarrow 2 / \left(\mathbf{K} \boldsymbol{\beta}^2 \ast \boldsymbol{\varepsilon} \right), \ \mathbf{a3} \rightarrow \dot{\mathbf{n}} \ast \boldsymbol{\omega} / \mathbf{K} \boldsymbol{\alpha}, \ \mathbf{a4} \rightarrow \dot{\mathbf{n}} \ast \boldsymbol{\omega} / \mathbf{K} \boldsymbol{\beta}, \ \mathbf{e1} \rightarrow \mathbf{Exp} [\mathbf{K} \boldsymbol{\alpha} \ast \mathbf{L}], \\ & \mathbf{e2} \rightarrow \mathbf{Exp} [-\mathbf{K} \boldsymbol{\alpha} \ast \mathbf{L}], \ \mathbf{e3} \rightarrow \mathbf{Exp} [\mathbf{K} \boldsymbol{\beta} \ast \mathbf{L}], \ \mathbf{e4} \rightarrow \mathbf{Exp} [-\mathbf{K} \boldsymbol{\beta} \ast \mathbf{L}], \ \mathbf{b1} \rightarrow \mathbf{Df} \ast \boldsymbol{\varepsilon} / \left(2 \ast \boldsymbol{\lambda}^2 \right) \right\}; \end{aligned}$

The simplified expressions of the integrations constants are asigned to the corresponding symbol, c1 - c6, and the known constants are inserted.

c1 = c1 /. sol2 /. const; c2 = c2 /. sol2 /. const; c3 = c3 /. sol2 /. const; c4 = c4 /. sol2 /. const; c5 = c5 /. sol2 /. const; c6 = c6 /. sol2 /. const;

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The expressions for $K\alpha$ and $K\beta$ are associated with the known constants:

Kα = Sqrt[$\dot{\mathbf{n}} * \boldsymbol{\omega} / Df$]; Kβ = Sqrt[$1/\lambda^2 + \dot{\mathbf{n}} * \boldsymbol{\omega} / Df$];

The potential ϕ is written as a function of distance, x, between the parallel walls.

 $phi[x_{]} := Re[-2/(K\beta^{2} * \epsilon) * (c3 * Exp[K\beta * x * \lambda] + c4 * Exp[-K\beta * x * \lambda]) + c5 * x * \lambda + c6]/(25 * 10^{4} - 3)$

 $\delta \rho$ p denotes the positive charge deviation, and $\delta \rho$ pn denotes the negative charge deviation.

```
\begin{split} &\delta\rho p[x_{-}] := \operatorname{Re}\left[c1 * \operatorname{Exp}\left[Ka * x * \lambda\right] + c2 * \operatorname{Exp}\left[-Ka * x * \lambda\right] + c3 * \operatorname{Exp}\left[K\beta * x * \lambda\right] + c4 * \operatorname{Exp}\left[-K\beta * x * \lambda\right]\right] \\ &\delta\rho n[x_{-}] := \operatorname{Re}\left[c1 * \operatorname{Exp}\left[Ka * x * \lambda\right] + c2 * \operatorname{Exp}\left[-Ka * x * \lambda\right] - c3 * \operatorname{Exp}\left[K\beta * x * \lambda\right] - c4 * \operatorname{Exp}\left[-K\beta * x * \lambda\right]\right] \end{split}
```

The following values are used as a starting point for the calculation:

$$\begin{split} \lambda &= 30 \pm 10^{-9}; \\ \varepsilon &= 78 \pm 8.85 \pm 10^{-12}; \\ \omega &= 10000; \\ Df &= 2 \pm 10^{-9}; \\ L &= 30 \pm \lambda; \\ V0 &= 0.01; \end{split}$$

The potential is plottet:

$Plot[phi[x], \{x, 0, L/\lambda\}, PlotRange \rightarrow All, AxesLabel \rightarrow \{ "x/\lambda ", "\phi/(k_BT/e)" \}];$]
and the charge deviations are plotted:	
$Plot[\delta\rho_{P}[x], \{x, 0, L/\lambda\}, PlotRange \rightarrow All, AxesLabel \rightarrow \{"x/\lambda", "\delta\rho"\}];$]
Plot[$\delta pn[x]$, {x, 0, L/ λ }, PlotRange $\rightarrow \lambda ll$];	2

A.2 Time dependent asymmetric solution

```
Clear["Global`*"];
Off[General::spell];
```

The six equations of the integration constants are contained in the following list named "eqs":

```
egs = {a1* (c1+c2) + a2* (c3+c4) + c6 == V0,
a1* (c1*e1+c2*e2) + a2* (c3*e3+c4*e4) + c5*L+c6 == -V0,
(c2-c1)*a3+ (c4-c3)*a4-c5*b1== 0, (c2*e2-c1*e1)*a3+ (c4*e4-c3*e3)*a4-c5*b1== 0,
(c1-c2)*a5+ (c3-c4)*a6+c5*b1== 0, (c1*e1-c2*e2)*a5+ (c3*e3-c4*e4)*a6+c5*b1== 0}
```

The equations are solved, and the simplified solution is stored in "sol2".

sol = Solve[eqs, {c1, c2, c3, c4, c5, c6}] // Flatten;

```
sol2 = Simplify[sol];
```

All the known constants (real and imaginary) used to reformulate the six equations are listed in "const".

```
\begin{aligned} \operatorname{const} &= \left\{ a\mathbf{1} \rightarrow \left( \dot{\mathbf{n}} \ast \omega / \left( \mathrm{Dp} \ast \mathrm{Ka}^2 \right) - 1 \right) \ast \left( 2 \ast \lambda^2 \right) / \varepsilon, \ a\mathbf{2} \rightarrow \left( \dot{\mathbf{n}} \ast \omega / \left( \mathrm{Dp} \ast \mathrm{K\beta}^2 \right) - 1 \right) \ast \left( 2 \ast \lambda^2 \right) / \varepsilon, \\ a\mathbf{3} \rightarrow \dot{\mathbf{n}} \ast \omega / \mathrm{Ka}, \ a\mathbf{4} \rightarrow \dot{\mathbf{n}} \ast \omega / \mathrm{K\beta}, \ a\mathbf{5} \rightarrow \mathrm{Ka} \ast \left( \dot{\mathbf{n}} \ast \omega \ast \mathrm{Dn} \ast \left( 1 / \mathrm{Ka}^2 - 2 \ast \lambda^2 \right) / \mathrm{Dp} + 2 \ast \mathrm{Dn} \ast \left( \lambda^2 \ast \mathrm{Ka}^2 - 1 \right) \right), \\ a\mathbf{6} \rightarrow \mathrm{K\beta} \ast \left( \dot{\mathbf{n}} \ast \omega \ast \mathrm{Dn} \ast \left( 1 / \mathrm{K\beta}^2 - 2 \ast \lambda^2 \right) / \mathrm{Dp} + 2 \ast \mathrm{Dn} \ast \left( \lambda^2 \ast \mathrm{K\beta}^2 - 1 \right) \right), \ e\mathbf{1} \rightarrow \mathrm{Exp} \left[ \mathrm{Ka} \ast \mathrm{L} \right], \\ e\mathbf{2} \rightarrow \mathrm{Exp} \left[ -\mathrm{Ka} \ast \mathrm{L} \right], \ e\mathbf{3} \rightarrow \mathrm{Exp} \left[ \mathrm{K\beta} \ast \mathrm{L} \right], \ e\mathbf{4} \rightarrow \mathrm{Exp} \left[ -\mathrm{K\beta} \ast \mathrm{L} \right], \ b\mathbf{1} \rightarrow \mathrm{Dp} \ast \varepsilon / \left( 2 \ast \lambda^2 \right) \right]; \end{aligned}
```

The simplified expressions of the integrations constants are asigned to the corresponding symbol, c1 - c6, and the known constants are inserted.

c1 = c1 /. sol2 /. const; c2 = c2 /. sol2 /. const; c3 = c3 /. sol2 /. const; c4 = c4 /. sol2 /. const; c5 = c5 /. sol2 /. const; c6 = c6 /. sol2 /. const; The expressions for $K\alpha$ and $K\beta$ are associated with the known constants:

 $\begin{aligned} & \text{K}\alpha = \text{Sgrt} \Big[1 / \left(2 * \lambda^2 \right) + \dot{n} * \omega * \left(1 / \text{Dn} + 1 / \text{Dp} \right) / 2 - \text{Sgrt} \Big[1 / \lambda^4 - \omega^2 * \left(1 / \text{Dn} - 1 / \text{Dp} \right)^2 \Big] / 2 \Big]; \\ & \text{K}\beta = \text{Sgrt} \Big[1 / \left(2 * \lambda^2 \right) + \dot{n} * \omega * \left(1 / \text{Dn} + 1 / \text{Dp} \right) / 2 + \text{Sgrt} \Big[1 / \lambda^4 - \omega^2 * \left(1 / \text{Dn} - 1 / \text{Dp} \right)^2 \Big] / 2 \Big]; \end{aligned}$

The following values are used as a starting point for the calculation:

$$\begin{split} \lambda &= 30 * 10^{-9}; \\ \varepsilon &= 78 * 8.85 * 10^{-12}; \\ \omega &= 100000; \\ Df &= 2 * 10^{-9}; \\ Dn &= 2 * 10^{-9}; \\ Dp &= 2 * 10^{-9}; \\ L &= 30 * \lambda; \\ V0 &= 0.01; \end{split}$$

A short check with the integrations constants for the symmetric time dependent solution:

{c3 ==	Df Kβ ² V0 ε		Df $e^{K_{BL}} K_{B}^{2} V0 \epsilon$
	2 Df (-1+ $e^{K\beta L}$) + \dot{n} (1+ $e^{K\beta L}$) K $\beta L \lambda^2 \omega'$		$\frac{1}{2 \operatorname{Df} (-1 + \operatorname{e}^{\mathrm{K} \mathrm{GL}}) + \operatorname{i} (1 + \operatorname{e}^{\mathrm{K} \mathrm{GL}}) \operatorname{K} \operatorname{f} \mathrm{L} \lambda^2 \omega}{2}$
-5	2 (1 + $e^{K\beta L}$) K β V0 $\lambda^2 \omega$		(1 + e ^{KβL}) KβL V0 λ ² ω
C3 ==	$\frac{1}{-2 \text{ in Df } (-1 + e^{K\beta L}) + (1 + e^{K\beta L}) K\beta L \lambda^2 \alpha}$) 00=	$\frac{1}{-2 \text{ in Df } (-1 + e^{K\beta L}) + (1 + e^{K\beta L}) K\beta L \lambda^2 \omega}$

{True, True, True, True}

The potential ϕ is written as a function of distance, x, between the parallel walls.

 $\begin{aligned} \phi[\mathbf{x}_{-}] &:= \\ &\text{Re}[(2*\lambda^{2} / \epsilon)*(\dot{\mathbf{n}}*\omega / (\mathbf{Dp}*\mathbf{K}\alpha^{2}) - 1)*(\mathbf{c}\mathbf{1}*\mathbf{Exp}[\mathbf{K}\alpha*\mathbf{x}*\lambda] + \mathbf{c}\mathbf{2}*\mathbf{Exp}[-\mathbf{K}\alpha*\mathbf{x}*\lambda]) + \\ &(2*\lambda^{2} / \epsilon)*(\dot{\mathbf{n}}*\omega / (\mathbf{Dp}*\mathbf{K}\beta^{2}) - 1)*(\mathbf{c}\mathbf{3}*\mathbf{Exp}[\mathbf{K}\beta*\mathbf{x}*\lambda] + \mathbf{c}\mathbf{4}*\mathbf{Exp}[-\mathbf{K}\beta*\mathbf{x}*\lambda]) + \mathbf{c}\mathbf{5}*\mathbf{x}*\lambda + \mathbf{c}\mathbf{6}] / \\ &(25*10^{\wedge}-3) \end{aligned}$

 $\delta \rho p$ denotes the positive charge deviation, and $\delta \rho pn$ denotes the negative charge deviation.

 $\begin{aligned} &\delta \rho p [x_{]} := \operatorname{Re} [c1 * \operatorname{Exp} [Ka * x * \lambda] + c2 * \operatorname{Exp} [-Ka * x * \lambda] + c3 * \operatorname{Exp} [K\beta * x * \lambda] + c4 * \operatorname{Exp} [-K\beta * x * \lambda]] \\ &\delta \rho n [x_{]} := \\ \operatorname{Re} [(1 + \dot{n} * 2 * \lambda^{2} * \omega / Dp - 2 * \lambda^{2} * Ka^{2}) * (c1 * \operatorname{Exp} [Ka * x * \lambda] + c2 * \operatorname{Exp} [-Ka * x * \lambda]) + (1 + \dot{n} * 2 * \lambda^{2} * \omega / Dp - 2 * \lambda^{2} * K\beta^{2}) * (c3 * \operatorname{Exp} [K\beta * x * \lambda] + c4 * \operatorname{Exp} [-K\beta * x * \lambda])] \end{aligned}$

Appendix B

Process flow





Drilling holes



B.1 Step by step process flow

Wafer containing channels

Step	Description					
0	Material					
	Pyrex wafers: 0.5 ± 0.05 mm thick.					
1	Cleaning					
	"Grammofonen" eller or ultra-sound bath for a rough cleaning.					
	Piranha / 7-up					
	Bake in 250°C for 2-3 hours or over night.					
2	Sputter deposition for anodic bonding (Varian)					
	(RF-clean and sputtering at 360°C.)					
	Plasma ashing, 1 ¹ / ₂ min, O ₂ : 210mL/min, N ₂ : 20mL/min, CF ₄ : 0, Power: 1000W					
	100 nm poly-Si at inward side of wafer.					
	Mask during HF etch and diffusion barrier during anodic bonding.					
3	Patterning of channels, mask 4					
	UV lithography – 2.2 μm resist AZ5214E, negative process					
	1. 5% HF etch (NOT bHF): app. 15 s.					
	Max. 2 hours before proceeding!					
	2. 2.2 μm resist on inward wafer side, pre-bake on hot-plate (2 min at 90 °C)					
	Track 1, recipe PR2_2.					
	3. Exposure. Negative process. Mask 4.					
	Hard contact. Exposure time: 4s					
	4. Reversal bake on hot-plate 120°C, time 2 min.					
	Track 2, recipe 2REV100, (120°C, 100s).					
	5. Flood exposure: 30 s (EV)					
	6. Develop: 60 s in AZ351B (NaOH)					
	Max. 40 min before proceeding with step 11!					
	Inspect wafer					
	Check lithography processes.					
4	Covering of wafer using blue tape					
	Inward wafer side (without resist) and wafer edges (use metal plate and scalpel).					
5	Wet etching of poly-Si defining etch mask for channels					
	[HNO ₃ :BHF:H ₂ O, 500:25:500], etch rate app. 100-400 nm/min with a magnetic stirrer.					
	Etch of 100 nm poly-Si on inward water side, app. 1.5 min (using a new mixture) or until					
	the channels become transparent.					
	Inspect wafer					
	Check poly-Si etch.					
0	Exching of channels					
	1 Used halos succession 120%C 25 min (Diverting is not down and)					
	1. Hard bake, oven 120°C, 25 min. (Blue tape is not damaged).					
	2. HF-etch, 40% HF, etch rate 3.2 μ m/min. (New solution: 3.4 μ m/min)					
	1 wo different etch distances: a) 50 μ m, b) 30 μ m					
7	5. Kinse 10-15 min in Di water.					
/	Sirip blue tape and resist in accione To quoid demoging the thin poly Si lower sectors is used to remove the blue tens					
	1 If necessary shift the holder using 4H gloves					
	 If increasing shift the noncer using 4Π-gloves. Dip in acetone for a couple of minutes until the blue tape loosens. 					
	2. Dry in account for a couple of minutes until the blue tape loosens. 3. Rinse shortly in DI water, take off the blue tape using AH gloves					
	A Rinse 5 min in DI water (Reneat if necessary the acatone bath)					
	4. Knise 5 min in Di water. (Kepeat in necessary the acetone datii).					
	J. Surpresist in actione and unit a-sound app. J lilli.					
	Check for resist leftovers					
	CHUCK IOI TOSISI IOIIOVOIS.					
Step	Description					
------	--					
0	Material					
	Pyrex wafers: 0.5 ± 0.05 mm thick.					
1	Cleaning					
	"Grammofonen" or ultra-sound bath for a rough cleaning.					
	Piranha / 7-up.					
	Bake in 250°C for 2-3 hours or over night.					
2	Metal deposition (Leybold)					
	Al 10 nm					
3	Patterning of electrodes, mask 1					
	UV lithography - 1.5um resist AZ5214E, negative process					
	1. 1.5 μm resist on inward wafer side, pre-bake on hot-plate.					
	Track 1, recipe PR1_5.					
	2. Exposure. Negative process. Mask 1.					
	Hard contact. Exposure time: 3s (EV).					
	3. Reversal bake on hot-plate: 120°C, 2 min.					
	Track 2, recipe 2REV100, (120°C, 100s).					
	4. Flood exposure: 30 s (EV).					
	5. Develop: 60 s in AZ351B (NaOH)					
	Inspect wafer					
	Check for resist and Al leftovers.					
4	Metal deposition (Alcatel)					
	Two different metals: a) 500 nm Al. b) 10 nm Ti + 500 nm Pt					
5	Lift-off					
	Lift-off in acetone (clean bath) with ultrasound (15-20 min), rinse in DI water.					
	Strip Al left-over in developer (NaOH). Might result in non-uniform electrode thicknesses.					
	Inspect wafer					
	Check quality of lift-off process and for Al leftovers.					

Wafer containing electrodes

Anodic bonding of the two wafers (poly-Si to pyrex glass)

Step	Description
1	Cleaning
	Piranha cleaning of channel wafer.
	Cleaning with compressed N ₂ gas of electrode wafer.
2	Alignment of channels and electrodes
3	Anodic bonding
	Use Si wafer with rough side up at the bottom electrode.

B.2 Equipment specifications

Metal/Si deposition:

- Leybold E beam evaporator, GMBH Dresden.
- Alcatel E beam evaporator, SCM 600.
- \bullet Silicon sputter deposition: Varian 3180 cassette sputtering system. Deposition at 360°C with an effect of $1.8\,{\rm kW}.$

Photolithography:

- Thin reversible photoresist: AZ5214E, Hverhst, New Jersey, USA.
- Thick positive photoresist: AZ4562E, Hverhst, New Jersey, USA.
- Spinning and prebake of resist: Semiconductor Systems Inc. spin coating and baking track.
- UV illumination: Electronic Visions co. contact aligner.
- Developer: AZ352B

Plasma ashing:

- Technics Plasma GMBH, Plasma- und Ionenstrahlsysteme, 300 Plasma Processor.
- Chamber cleaning process at 1000 W: 30 min with gas flows; 220 mL/min N_2 , 500 mL/min O_2 and 0 mL/min CF_4 .
- Wafer cleaning process at 1000 W: 210 mL/min O₂, 20 mL/min N₂, 0 mL/min CF₄.

Drilling holes:

• Cylindrical diamond drill: DanDental A/S, Denmark.

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Appendix C

Process flow for etched inlet holes



C.1 Step by step process flow

Wafer containing channels

Step	Description
0	Material
	Pyrex wafers: 0.5 ± 0.05 mm thick.
1	Cleaning
	"Grammofonen" eller or ultra-sound bath for a rough cleaning.
	Piranha / 7-up
	Bake in 250°C for 2-3 hours or over night.
2	Measure wafer thicknesses (Sylvac)
	To obtain the correct etch times.
3	Sputter deposition for mask during HF etch (Varian)
	(RF-clean and sputtering at 360°C)
	Plasma ashing, 1 ¹ / ₂ min, O ₂ : 210mL/min, N ₂ : 20mL/min, CF ₄ : 0, Power: 1000W
	1000 nm = 1 μ m poly-Si at outward side of wafer.
	Max. 2 hours before proceeding!
4	Patterning of in- and out-let holes, mask 3
	UV lithography – 9.5 μm AZ4562, positive process
	1. 9.5 μm resist on outward wafer side, pre-bake on hot-plate (3min. at 90 °C).
	Track 2, recipe PR9_5.
	Wait at least 1.5 hours before exposure!
	2. Exposure. Positive process. Mask 3.
	Hard contact. Exposure time: 50s (EV aligner).
	3. Develop: 4.5 min in AZ351B (NaOH)
	Max. 40 min before proceeding with step 6!
	Inspect wafer
	Check lithography process.
5	Covering of wafer using blue tape
	Inward wafer side (without resist) and wafer edges (use metal plate and scalpel).
6	Wet etching of poly-Si defining etch mask for in- and out-let holes
	[HNO ₃ :BHF:H ₂ O, 500:25:500], etch rate app. 100-400 nm/min with a magnetic stirrer.
	Etch of 1 μ m poly-Si, 3-5 min (using a new mixture) – 5min is enough.
	Rinse thoroughly in DI water.
	Inspect wafer
	Check poly-Si etch.
7	Etching of in- and out-let holes
	Process the wafers one at a time: Max 2 hours from hard bake until etching!
	(Make sure not to etch all the way through the wafer.)
	1. Cover alignment marks with blue tape.
	2. Hard bake, oven 120°C, 25 min. (Blue tape is not damaged).
	3. HF-etch, 40% HF, etch rate 3.2 μ m/min with a magnetic stirrer.
	Total etch distance: Wafer thickness – 2*channel height
	4. Rinse for 15 min in DI water before proceeding with the acetone.
8	Strip blue tape and resist in acetone
	1. If necessary shift the holder using 4H-gloves.
	2. Dip in acetone for a couple of minutes until the blue tape loosens.
	3. Rinse shortly in DI water, take off the blue tape using 4H-gloves.
	4. Rinse 5 min in DI water. (Repeat if necessary the acetone bath).
	5. Strip resist in acetone and ultra-sound app. 5 min.
	Inspect wafer
	Check for resist leftovers.

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C.1. STEP BY STEP PROCESS FLOW

9	Sputter deposition for anodic bonding (Varian)
	(RF-clean and sputtering at 360°C.)
	Plasma ashing, 1 ¹ / ₂ min, O ₂ : 210mL/min, N ₂ : 20mL/min, CF ₄ : 0, Power: 1000W
	100 nm poly-Si at inward side of wafer.
	Mask during HF etch and diffusion barrier during anodic bonding.
10	Patterning of channels, mask 4
	UV lithography – 2.2 μm resist AZ5214E, negative process
	1. 5% HF etch (NOT bHF): app. 15 s.
	Max. 2 hours before proceeding!
	2. 2.2 μm resist on inward wafer side, pre-bake on hot-plate (2 min at 90 °C)
	Track 1, recipe PR2_2.
	3. Exposure. Negative process. Mask 4.
	Hard contact. Exposure time: 4s
	4. Reversal bake on hot-plate 120°C, time 2 min.
	Track 2, recipe 2REV100, (120°C, 100s).
	5. Flood exposure: 30 s (EV)
	6. Develop: 60 s in AZ351B (NaOH)
	Max. 40 min before proceeding with step 11!
	Inspect wafer
	Check lithography processes.
11	Wet etching of poly-Si defining etch mask for channels and removing the thick
	outward layer
	[HNO ₃ :BHF:H ₂ O, 500:25:500], etch rate app. 100-400 nm/min with a magnetic stirrer.
	Etch of 100 nm poly-Si on inward wafer side and 1 µm poly-Si on outward wafer side,
	app. 2.5 min (using a new mixture) or until the thick poly-Si layer is removed and the
	channels become transparent.
	Inspect wafer
	Check poly-Si etch.
12	Etching of channels
	Process the wafers one at a time: Max 2 hours from hard bake until etching!
	1. Hard bake, hot-plate 120°C, 2 min.
	2. HF-etch, 40% HF, etch rate 3.2μ m/min. (New solution: 3.4μ m/min)
	Two different etch distances: a) 50 μ m, b) 30 μ m
	3. Rinse 10-15 min in DI water.
13	Strip resist in acetone
	Inspect wafer. Measure channel depth with Dektak.

Chemicals should be mixed just before use. Poly-Si etch changes overnight, HNO_3 evaporates. HF etch-rate changes as well.

Appendix D

Instruments

Specifications of the equipment used for measurements of hydraulic resistance, impedance spectra and fluid velocity.

- Ministac fittings: Upchurch Scientific, M-644-03 and M-647.
- Latex tubes, 1/16" $\times 0.5$ mm.
- O-rings: Geometry adopted from Upchurch Nanoports.
- Lock-In Amplifier: Model SR830DSP. Stanford Research Systems.
- 16-bit data acquisition card: National instruments, Austin, TX, USA.
- Electroactuated valves: Lee Company, Westbrook, CT, USA.
- Pressure sensors: Honeywell 40PC150G1A, Freeport, IL, USA.
- Balance. 0.1 mg precision Sartorius CP224S, Goettingen, Germany.
- Impedance Analyzer: Impedance/Gain-Phase Analyzer HP 4194 A.
- Fluorescent beads, 4 μm: FluoSpheres F-8859, Lot 6901-3, sulfate microspheres, yellow-green fluorescent (505/515). Molecular Probes, Eugene, Oregon, USA.
- Fluorescent beads, 1 μm: FluoSpheres F-8765, Lot 6902-1, amine-modified microspheres, yellow-green fluorescent (505/515). Molecular Probes, Eugene, Oregon, USA.
- \bullet Syringe filters: $0.45\,\mu\mathrm{m}$ polyether sulfane Membrane, cat. nr. 6781-2504. Whatman Inc.
- Stereo microscope and camera: Leica MZFLIII Microscope. Sony DFW-X710 Color Digital Camera.
- Conductivity meter: MeterLab CDM210, Radiometer, Copenhagen.

Appendix E

p-Q characteristics

E.1 Labview

Labview program used to control the p-Q measurement and collect data.



Figure E.1: Front Panel used to control the measurement parameters.



Figure E.2: Block diagram of the Labview program. Here the components of the measurement setup are directly represented as icons, and the code to control the measurement procedure is written.

E.2 Plot *p*-*Q* characteristics

Matlab program to plot p-Q diagram from the acquired data file during measurements. The output is a plot of the measured p-Q values fitted linearly in order to determine the hydraulic resistance of the system.

```
% Plotting P-Q characteristic
% Department of Micro and Nanotechnology 2005
% by Misha Gregersen (Modified file from ABR)
clear all
close all
clear A;
filename='ca753';
ti=5; %transition cut in data
rho=1; %mg/uL
fid=fopen(filename); %The file is opened in read mode.
i=1;
while 1
    tline = fgetl(fid);
                                  Returnes the next line of "fid".
    if tline==-1 break; end
                                  %-1 if end-of-file indicator is reached.
    tline = strrep(tline,',','.'); %Replaces , with .
    A(i,:)=str2num(tline);
                                 *Converting to numeric representation.
    i=i+1;
end
fclose(fid);
[rows c]=size(A); 🐁
A=A(1:end-1,:); %last row of data set is removed (resetting)
p=A(:,1); %pressure state
m=A(:,2); %mg
p1=A(:,3); %bar
p2=A(:,4); %bar
dp=A(:,5); %bar
t=A(:,6); %s
```

```
maxstate=max(p);
for i=0:maxstate
Ivec=find(p==i);
Ivec=Ivec(ti:end-ti);
Mfit=polyfit(Ivec,m(Ivec),1); %mg/s
Qm(i+1) = (1/rho) *Mfit(1); %muL/s
Pm(i+1) = mean(dp(Ivec)); %bar
end
%Qm is the mean flow volume/second for a given pressure difference
% (pressure state) .
%Pm is the mean pressure difference for a given pressure state.
%The measurement vectors are transposed.
PmO = [Pm(:)'];
QmO = [Qm(:)'];
Qfit=polyfit(Pm0,Qm0,1);
%Conversion from hyd. cond. [muL/s/bar] to hyd. res. [Pa s/m^3].
display(Qfit)
Rhyd=1/(Qfit(1)*10^(-14));
sprintf('Rhyd = %e (Pa s)/m^3',Rhyd)
figure(1);
hold on
plot(Pm0,Qm0,'kx');
xx = linspace(0,PmO(end),80);
Pfit=polyval(Qfit,xx);
plot(xx, Pfit);
xlabel('pressure drop [bar]');
ylabel('Flow [\muL/s]')
legend('Data points',sprintf('Q = %.3gp %.2g',[Qfit]),'Location', 'best')
title(sprintf('%s',filename)) %The filename is printed in the title.
grid on
```

hold off

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