Pressure Driven Transport in Nanofluidic Channels

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When I started in the group of Molecular Biophysics (MB) about four and a half years ago, it was quite a small group that had just been split off from QT (Quantum Transport). It is hard to imagine now that I was only the second PhD student to start his project in MB. During my time as a PhD student, MB has grown tremendously, attracting many talented people and earning a solid reputation in the field of bionanotechnology. It was exciting to be a part of it.

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Frank van der Heyden
Delft, December 2006
# Contents

1 Introduction ........................................... 7
   1.1 Nanofluidics ........................................ 8
   1.2 Outline of this Thesis .............................. 15
       References ......................................... 17

2 Theoretical Concepts .................................. 19
   2.1 The Double Layer .................................... 20
   2.2 Fluid and Ion Transport ............................ 21
   2.3 Charge Inversion .................................... 28
   2.4 DNA Polymers in Confinement ...................... 34
   2.5 Taylor Dispersion in a Slit-like Geometry ........ 39
       References ......................................... 41

3 Streaming Currents in a Single Nanofluidic Channel 45
   3.1 Introduction ......................................... 46
   3.2 Device Fabrication & Methods ....................... 46
   3.3 Measurements of the Streaming Current ............ 48
   3.4 Models of the Electrical Surface Properties .... 48
   3.5 Model Comparison & Discussion .................... 51
   3.6 Conclusion .......................................... 53
       References ......................................... 53

4 Charge Inversion at High Ionic Strength .............. 55
   4.1 Introduction ......................................... 56
   4.2 Device Fabrication & Methods ....................... 56
   4.3 Charge Inversion by Trivalent Ions ................. 57
   4.4 Charge Inversion by Divalent Ions ................ 60
   4.5 The Effect of Monovalent Salt on Charge Inversion 62
   4.6 Conclusion .......................................... 64
References .................................................. 64

5 Theory of Electrokinetic Power Generation 67
  5.1 Introduction ............................................. 68
  5.2 The Efficiency of a Fluidic Device of Arbitrary Geometry .... 70
  5.3 Calculations for a Slit-Like Nanochannel ................... 71
  5.4 The Limit of Strong Double-Layer Overlap ................. 74
  5.5 The Electrical Output Power of a Macroscopic Device ....... 79
  5.6 Conclusions ............................................ 79
  5.7 Appendix A - The Onsager Relation ....................... 80
  5.8 Appendix B - Ions of Arbitrary Valence ................... 82
References .................................................. 87

6 Experiments on Electrokinetic Power Generation 89
  6.1 Introduction ............................................. 90
  6.2 Device Fabrication & Methods .......................... 91
  6.3 The Effect of the Load Resistor ......................... 91
  6.4 The Salt Concentration and Channel Height Dependence .. 94
  6.5 Stern Conductance ..................................... 96
  6.6 Conclusions ............................................ 97
References .................................................. 97

7 Pressure-Driven Transport of Confined DNA 101
  7.1 Introduction ............................................. 102
  7.2 Materials and Methods .................................. 103
  7.3 DNA Velocity in Confined Fluidic Channels ............... 104
  7.4 The Statistical Polymer Distribution Model ............... 107
  7.5 DNA Dispersion in Confined Channels .................... 110
  7.6 Conclusions ............................................ 113
References .................................................. 114

Summary ................................................... 117
Samenvatting ............................................... 121
Curriculum Vitae .......................................... 125
List of Publications ....................................... 127
Chapter 1

Introduction

This chapter introduces the field of nanofluidics, where fluids are confined and manipulated at the nanoscale. An overview is given of the fundamentally new regimes that become available when fluidic systems are miniaturized into the nanoregime, and some inspiring recent experiments are presented to highlight the new possibilities of this field. Where relevant, we make connections to the experimental work which constitutes the main part of this thesis. This introduction ends with a brief description of each chapter.
1.1 Nanofluidics

Nanofluidics refers to the study and application of fluid flow in and around nano-sized objects [1, 2]. Nanofluidic effects have long been studied in disciplines such as colloid science and biology, where interactions between (charged) objects in an aqueous environment at the nanoscale are important [3–6]. The field of nanofluidics recently acquired renewed interest with the invention and wide availability of many new technological tools, both for fabrication and inspection [7–19]. Miniaturization of microfluidics into the nano regime not only promises quantitative improvements, such as the use of less reagents and solvents, massively parallel analysis, faster operation, less power consumption and increased opportunities for integration. Nanofluidics also offers qualitatively new possibilities, when the length scales of the devices start to overlap with the typical dimensions of electrical double layers, biological macromolecules, or even molecules and ions (Fig. 1.1). The rest of this section provides an overview and examples of the new science and novel applications that can be expected when we enter these fundamentally different regimes.

i) Double Layer Overlap

Charged surfaces in liquids are electrostatically screened by a layer of counterions, the so-called double layer. The thickness of this double layer, ranging from 1 nm at high salt to 100 nm at low salt, defines the length scale at which electrostatic forces are mediated. In nanofluidic channels with charged walls, ions of the same charge (co-ions) are repelled when double layers overlap, resulting in solutions containing only one type of ions, and enabling the design of ion filters. Semi-permeable membranes and in particular biological pores illustrate the high selectivity that can potentially be achieved, if the local electrostatic environment and geometry inside the pores can be designed and optimized in detail. Solid-state ion filters have not reached that level of selectivity yet, but novel filtering principles, such as conically shaped ratchets, have recently been demonstrated [20]. Electrostatic gates can be integrated in fabricated structures to actively control and even reverse the surface charge [19, 21]. This allows the switching of ion filters, and more generally opens up a whole new range of possibilities of electrostatic manipulation and detection of charged objects such as proteins and DNA polymers in nanofluidic structures where double layers overlap. Nanofluidic channels can also be used to generate electrical power through streaming currents: the pressure-driven transport of counterions in the nanochannel. We discovered that this process becomes particularly efficient when double layers overlap (see Chapter 5 and 6 of this thesis).
1.1 Nanofluidics

DNA size scales

- base size
- DNA width
- persistence length
- contour length
- radius of gyration

other objects

- molecules
- proteins
- viruses
- cells

screening length

monovalent salt concentration:
- 1M
- 1mM
- 1μM

1 nm 10 nm 100 nm 1 μm 10 μm

UV lithography
nanoimprint lithography
e-beam lithography
scanning probe lithography
solid-state pores
Bottom-up
molecular assembly
Top-down

Figure 1.1: The length scales of the fundamental building blocks of biology and electrostatic screening overlap with the length scales realizable using micro- and nanofabrication technology [2]. Typical size scales are indicated for double stranded DNA (base size ~ 0.3 nm; width ~ 2 nm; persistence length ~ 50 nm for standard physiological conditions). For DNA in the range 4–50 kbp, the radius of gyration is 0.2–0.7 μm and the contour length 1.5–16 μm. The screening length is calculated for monovalent salt in aqueous solution, where the dissociation of water molecules prohibits concentrations below ~ 1μM. Top-down fabrication methods include UV-lithography, nano-imprint technology [10], E-beam lithography, and scanning probe lithography [11]. It is also possible to fabricate pores down to a few nanometers in thin membranes using ion or electron-beams [12, 13]. Bottom-up approaches include the self-assembly of smaller units of organic materials into pores [14], channels [15], or even larger structures [16, 17], and the use of carbon nanotubes or nanowires as fluidic channels [18, 19].
ii) Small Volumes

Small volumes increase the sensitivity for detecting small signals due to a reduction of background noise from the bulk. Examples are the possibility of measuring current blockades during DNA translocations through small pores at high salt [12, 23, 24] and sensitive single-molecule fluorescence measurements with a large background fluorescence (Fig. 1.2, ref. [22]). Also, the electrical conductance of surfaces can be accurately measured when the bulk conductance is small, i.e., in small channels and at low salt concentrations [25]. This principle was employed to detect DNA translocations through nanopores at low salt through a peak in conductance [26]. The detection of streaming currents (Chapter 3 and 4) also benefits from small channel volumes, as the bulk fluid in the center of large channels does not add to the streaming current signal, but causes an extra conductive background current when electrode potentials drift.

Different physical processes and forces start to dominate when dimensions shrink, which may be exploited in the design of nanofluidic devices. Examples include the fast diffusion across nanofluidic structures leading to efficient mixing (a persistent problem in microfluidics), the absence of thermal gradients, and the possibility of rapid heating and cooling which can be employed to create and study novel chemical reactions. While forces such as gravity, inertia and buoyancy play an important role in macroscopic systems [1, 27], viscous and surface forces dominate in the microfluidic regime, and this only becomes more pronounced for nanofluidics. A result is that fluid flows in micro- and nanofluidic devices are always laminar. Surface effects in two-phase flows have been effectively employed to transport liquids in microfluidic channels by either actively changing the wetting properties of the surface by electrostatic methods [28] or by a clever design.
in channel height variations [29]. Other applications of surface-tension effects in microscale geometries include breathable waterproof fabrics such as gore-tex which rely on small hydrophobic pores in a membrane, self-cleaning surfaces (the "lotus-effect", [30, 31]) and the harvesting of morning fog on beetle wings for drinking [32]. When dimensions shrink into the nanoregime, surface-energy-driven fluid transport can generate increasingly large pressures. For example, a negative pressure as high as $-17$ bar was observed in a hydrophilic $\sim 100$ nm-high channel partly filled with water [33].

iii) Spatial Confinement

Probably the most imaginative and interesting new regime of nanofluidics, is the situation where the physical size of the channel geometry becomes comparable or smaller than the size of the object under investigation. Several fundamentally new mechanisms for the separation of biopolymers and beads have recently been experimentally demonstrated [34–36]. For biopolymers such as DNA, an even wider array of separation and trapping possibilities exist [37–40] as they may be forced into geometries smaller than their typical size given by the radius of gyration $R_g$. We will discuss a few recent experiments that highlight the new possibilities of this field.

The first set of separation experiments have made clever use of the possibility to engineer fluid flows and local velocity gradients at the scale of the particles to be separated. The most straightforward of these are the separations based on hydrodynamic chromatography (HDC). The HDC separation principle relies on the size-dependent exclusion from the wall in a channel in which a pressure-driven flow is applied [41]. The corresponding flow profile results in a larger velocity for larger analytes, since they will on average spend more time in the faster flowing

![Figure 1.3](image)

**Figure 1.3:** Schematic illustration of the two regimes of pressure-driven transport of a biopolymer [34]: a) The channel is bigger than the radius of gyration of the polymer, representing the 'HDC'-regime, where the mobility increases with the polymer size. The molecule’s center of mass is excluded from the channel wall, inducing large molecules to spend a greater amount of time in the central, high-velocity region of the fluid flow. b) When the polymers are confined to a narrow channel, their mass distribution across the channel height and mobility become essentially independent of the polymer length.
regions in the center of the channel (Fig. 1.3a). For well-defined geometries, such as capillaries or slit-like channels, the pressure-driven laminar flow profile can lead to very efficient separations [41]. Recent experimental demonstrations of this effect include the separation of beads and biopolymers in microchannels [35] and our experiments on the mobility of pressure-driven DNA-molecules in nanochannels (Chapter 7, [34]). When the nanochannel is smaller than $R_g$, the effects of HDC vanish and all polymers elute with the same velocity (Fig. 1.3b).

Another creative approach for the separation of nanoparticles has recently been presented by Huang et al. [36], and is illustrated in Fig. 1.4. A fluid flow was applied across an array of fabricated pillars, where the position of each row of pillars was slightly shifted with respect to the previous row. The fluid flow meanders through this structure in a well-defined manner (Fig. 1.4b). Small particles are able to follow the fluid streamlines exactly, but large particles can only pass between the pillars through the middle, and are systematically displaced into one particular direction (Fig. 1.4c). This deterministic size-dependent displacement can be employed in a separation device.

Another category of novel separation principles makes use of entropic forces. When a polymer sits at the boundary of a shallow ($< R_g$) and a deep ($> R_g$) channel region, it experiences an entropic force towards the deep area as the polymer strives to keep its equilibrium conformation [37, 38], as illustrated in Fig. 1.5b. Balancing this entropic force with the hydrodynamic drag of an applied

![Figure 1.4](https://example.com/figure1.4.png)

**Figure 1.4**: a) A fluid flow is applied across an obstacle matrix in the vertical direction (large arrow) [36]. b) Three fluid streams in a gap do not mix as they flow through the matrix. Lane 1 at the first obstacle row becomes lane 3 at the second row, lane 3 becomes lane 2 at the third row, and so on. Small particles follow the streamlines and will thus flow from the top to the bottom. c) A particle with a radius that is larger than lane 1 follows the streamline of line 2 passing through the center of the particle (black dot). The particle is consistently displaced towards the right as it enters the next gap.
1.1 Nanofluidics

Fluid flow results in an average stalling time of the polymer at the interface, which decreases with polymer length (Fig. 1.5c). This principle can be used for separation, in particular when a long array of entropic traps is used (Fig. 1.5a).

A second way to effectively harness the entropic force in a separation device was presented by Turner et al. [39, 40]. A mixture of DNA polymers with different lengths in a channel deep enough for them to retain their equilibrium $R_g$ were electrophoretically driven into an area with narrow pillars, forcing them to stretch out at an entropic cost (Fig. 1.6a). After a certain amount of time, the driving field was switched off. Short molecules were completely driven into the pillared region and remained there, while long molecules were still partly in the deep region and started recoiling to their original equilibrium conformation, thereby retracting the stretched part from the pillared region (Fig. 1.6b). This process of switching on and off the field can be repeated, for example, to first separate the shortest molecules and then the longer ones by gradually increasing the switching time.

**Figure 1.5:** a) Side view of a nanofluidic separation device with many entropic traps [38]. b) Cross-sectional schematic diagram of the device. Electrophoresed DNA molecules are trapped whenever they meet a shallow region, because their radius of gyration is much larger than the shallow region depth. c) Top view of the device in operation. Trapped DNA molecules eventually escape. Larger molecules have a higher escape probability because they cover a wider region of the slit ($w_{\text{large}} > w_{\text{small}}$).
iv) Nanofluidics at the Molecular Size Scale
Recent experiments of water enclosed in $1 - 10 \text{ nm}$ diameter carbon nanotubes revealed anomalous behavior and widely diverging results, such as a greatly retarded fluid mobility [42], hydrophilic carbon [43], unstable pulse-like fluid motions [44] and fast mass transport [18]. Molecular dynamics simulations for water transport in such systems yielded equally unexpected results, such as the pulse-like transmission of water through the nanotube (Fig. 1.7, ref. [45]) and charge inversion by monovalent ions [46]. The above mentioned counterintuitive phenomena are not explained by classical continuum theory, but can only be accounted for when the molecular nature of water and ions is considered. Another manifestation of the breakdown of continuum theory is the surprisingly high stability of $1 - 10 \text{ nm}$ diameter nanobubbles, which according to continuum theory should dissolve due to the very high surface tensions at this scale [47]. Still very little is known about the behavior of fluids in these small dimensions and its underlying mechanisms.
1.2 Outline of this Thesis

In this thesis, we report experiments on the pressure-driven transport of ions and DNA polymers in rectangular fluidic channels made from silica in the range of 70 – 1000 nm. We first discuss in Chapter 2 the theoretical background that is needed to understand and appreciate the experiments that are presented in the rest of the thesis. In this chapter, we treat the theory of electrical double layers in some detail, and describe how the double layer is related to electrokinetic effects such as streaming currents. This chapter also discusses the effects of ion correlations in the Stern layer, which can lead to a sign-reversal of the effective surface charge in the presence of multivalent ions. We then present some basics of polymer physics, and describe the statistical distribution of DNA in confinement. We end with a discussion on Taylor dispersion in rectangular channels.

In Chapter 3, we report streaming current measurements in individual silica nanochannels. These measurements allow for the quantitative investigation of the silica surface charge, due to the well-defined geometry and high surface-to-volume ratio of the nanochannels. We studied the effective surface charge of silica as function of monovalent salt concentration and channel height. A constant zeta potential completely failed to describe the silica surface. A constant surface charge modeled our streaming current results well at low salt, but not across the full salt range. The surface charge of silica was best described by a model that takes into account the chemical equilibrium of the charge-determining silanol groups at the surface. These quantitative results up to high salt concentrations highlight the appropriate electrical boundary conditions for silica in nanofluidic channels.

In Chapter 4, we studied the effective surface charge in the presence of multivalent ions using streaming currents. Multivalent ions can cause the surface charge to flip sign under certain conditions. For trivalent and tetravalent ions,
this effect is well-studied as it occurs at relatively low concentrations. We report measurements of charge inversion at high ionic strength in the largely unstudied regimes of divalent ions, and for higher valency ions with added monovalent salt. Charge inversion was found occur at high concentrations of divalent ions. Monovalent salt suppressed charge inversion by trivalent ions, which could be modeled within the framework of ion correlation theory by including the effects of screening, and taking the entropy of mixing into account.

Chapter 5 theoretically discusses the limits and possibilities of employing electrokinetic effects to generate electrical power. We used classical continuum theories to model the charge distribution and fluid flow in slit-like nanochannels with a constant surface charge at the walls, and found the conditions that yield the highest energy conversion efficiency: The optimal efficiency is obtained when double layers overlap (at low salt in nanoscale channels), when the surface charge has a particular value inversely proportional to the channel height, and when the ions have a low mobility. The highest efficiency that is predicted for potassium ions in water is approximately 7%.

In Chapter 6, we report measurements of the electrokinetic energy conversion efficiency in slit-like nanochannels that test the theoretical predictions of Chapter 5. The regime of double layer overlap was indeed found to yield the highest efficiencies: up to $\sim 3\%$ in a 75 nm-high channel, the smallest channel measured. The measured efficiencies were however lower than those calculated, because of the presence of an extra conductance in the Stern layer at the silica surface, which provides an additional pathway for power dissipation. Remarkably, the Stern conductance was found to be the same for ions with a very different bulk mobility which suggests that protons dominate the conductance in the Stern layer. Reducing the Stern conductance should improve the efficiency in future experiments.

Chapter 7 presents an investigation of the pressure-driven mobility and dispersion of individual DNA molecules in micro- and nanofluidic channels. Measurements on the DNA mobility revealed both length-dependent and length-independent regimes, and the crossover channel height between these two regimes increased with molecular length. This behavior can be explained by the statistical distribution of DNA molecules in slit-like nanochannels, modeled using equilibrium random-flight statistics. The Taylor dispersion and the self-diffusion of DNA are observed to be strongly reduced in confined channels. We present scaling relationships that capture our observations. The observed Taylor dispersion could not be predicted by conventional point-like or rigid particle-models, and must be rooted in the statistical properties of the DNA polymer.
References


Chapter 2

Theoretical Concepts

This chapter discusses the theoretical concepts that underlie much of the experimental work in the rest of this thesis. We start by describing the structure of the electrical double layer, a layer of net charge in the fluid that screens the charge of the surface. The motion of this net charge in the double layer is coupled to the motion of the fluid, which causes so-called electrokinetic effects. The mean-field equations that govern the ion distribution in the double layer and its coupling to the fluid flow are discussed. This is followed by a description of the theory of the strongly correlated liquid, which predicts that multivalent ions accumulate in a two-dimensional-like lattice structure adjacent to a charged surface. The effect of charge inversion occurs, when so many of these multivalent ions accumulate that the surface charge effectively changes sign. We then describe some basics of polymer theory and discuss the distribution of the polymer segments in free solution and in confinement. We end this chapter with the theory of point-like particle dispersion in slit-like channels.
2.1 The Double Layer

The concept of the double layer arose in the work of Von Helmholtz [1] on the interfaces of colloidal suspensions. It was subsequently extended to surfaces of metal electrodes by Gouy [2], Chapman [3], Stern [4], and Grahame [5]. The various models of the double layer are shown in Figure 2.1. Helmholtz envisaged a capacitor-like separation between the surface charge of the colloidal particle and a compact layer of countercharges in the electrolyte. Gouy and Chapman introduced a diffuse model of the electrical double layer, which typically extends much further into the liquid than the Helmholtz layer. Stern combined both models into the Stern-Gouy-Chapman model. Further refinements to the compact Helmholtz layer, also called the Stern layer, were made by Grahame, and later by many others [6]. These refinements have led to a plethora of fit parameters, such as the position of inner and outer Helmholtz planes, inner and outer dielectric constants, chemical binding constants, hydration energies, and so on [7]. Although these refined models of the double layer often described experimental results well, their predictive power has remained poor and the physical meaning of the fitted parameters questionable. Moreover, ageing and contamination of surfaces in contact with liquid [8], and variations between nominally identical surfaces [9] makes experimental verification of the subtleties in such models difficult. Therefore, a simple model that focuses on the dominant effects with only a few fit parameters is preferable.

In this thesis, we describe the electrical double layer using the Stern-Gouy-Chapman model. The no-slip plane and the electrical surface charge or potential - which represent the boundary conditions for the fluid flow and the diffuse layer, respectively - are taken to be at the interface between the Stern and the diffuse layer. While the liquid between the no-slip plane and the surface is immobile, the ions in the Stern layer are assumed to still have a finite mobility when electrical fields are applied [10]. The Stern layer can therefore be modeled as an electrical conductance, the Stern conductance. The electrophoretic motion of the ions behind the no-slip plane is presumably not coupled to the surrounding liquid. The electrostatic potential and charge distribution in the diffuse layer are described by the well-known Poisson-Boltzmann equation, which generally yields nonlinear solutions. For a low surface potential, $\zeta$, the Poisson-Boltzmann equation can be linearized, yielding the well-known Debye-Hückel approximation. This approximation predicts an exponential decay of the potential $\phi$ with distance $d$ from the surface, $\phi = \zeta \exp(-\kappa d)$, where $1/\kappa$ is the Debye screening length. In this thesis, we will not use the Debye-Hückel approximation, but instead use full nonlinear solutions to the Poisson-Boltzmann equation.
2.2 Fluid and Ion Transport

In this section, we present the Poisson-Nernst-Planck (PNP) equations that govern the fluid and ion transport in the diffuse layer. We show that the Poisson-Boltzmann (PB) equation for the electrostatic charge distribution follows directly from these general equations for fluidic systems in thermodynamic equilibrium. We solve PNP for low Reynolds numbers in the parallel-plate geometry with an applied pressure and potential gradient, and we present expressions for the linear electrokinetic response properties for such as system.
Governing Equations

We define a local pressure $p$, electrostatic potential $\phi$, charge density $\rho$ and fluid velocity $u$ at position $x$ in the fluid. The fluid is of constant density $\rho$ and viscosity $\eta$, and taken to be incompressible:

$$\nabla \cdot u = 0 \quad (2.1)$$

With these assumptions, the motion of the fluid is described by the Navier-Stokes equation [11],

$$\rho \left[ \frac{\partial u}{\partial t} + (u \cdot \nabla) u \right] = -\nabla p - \rho \nabla \phi + \rho \mathbf{g} + \eta \nabla^2 u \quad (2.2)$$

where $\mathbf{g}$ is the acceleration due to gravity. The four terms on the right hand side represent the forces on a small volume element due to the pressure gradient, the electrical field, gravity, and viscous friction, respectively. The Navier-Stokes equation results from Euler’s equation of motion by adding the viscous force [11].

The charge density is related to the potential through Poisson’s equation

$$\rho = -\epsilon \epsilon_0 \nabla^2 \phi \quad (2.3)$$

where $\epsilon \epsilon_0$ is the permittivity of the fluid. The electrolyte contains several ionic species $i$ with electrophoretic mobility $\mu_i$, signed valence $Z_i$, and local number density $n_i(x)$, which define $\rho = \sum Z_i e n_i$ with $e$ the electron charge. Each ion species obeys a conservation equation

$$\frac{\partial n_i}{\partial t} + \nabla \cdot \mathbf{j}_i = 0 \quad (2.4)$$

where the flux vector $\mathbf{j}_i$ is defined by the Nernst-Planck equation for ion transport

$$\mathbf{j}_i = -\mu_i n_i \nabla \phi - D_i \nabla n_i + n_i u = -\frac{\mu_i n_i}{Z_i e} \nabla U_i + n_i u \quad (2.5)$$

where $D_i = \frac{kT \mu_i}{Z_i e}$ is the diffusivity defined by Einstein’s relation, $kT$ the thermal energy, and $U_i = Z_i e \phi + kT \ln n_i$ the chemical potential.
Boundary Conditions

The boundary conditions are those of no slip at the wall and zero ion flux normal to the wall:

\[ u = 0, \quad \text{and} \]
\[ j_i \cdot n = 0 \]  

(2.6)  

(2.7)

where \( n \) is the unit normal directed into the fluid. We can either take an electrostatic potential \( \zeta \) or a surface charge density \( \sigma \) as the electrical boundary condition for the surface:

\[ \phi = \zeta, \quad \text{or} \]
\[ -\nabla \phi \cdot n = \frac{\sigma}{\varepsilon \varepsilon_0} \]  

(2.8)  

(2.9)

For the general case, \( \sigma \) and \( \zeta \) do not have to be constants: they may vary along the channel surface, or can be described as a chemical equilibrium [12] allowing for effects such as charge regulation. We assume that ions do not move across the interface between the Stern layer and the diffuse layer (Eq. 2.7), and that the electrical boundary conditions are defined at this interface. These assumptions imply that whatever happens within the Stern layer has no effect on our calculations of the electrokinetic effects in the diffuse layer. If the non-steady-state behavior is calculated, the initial distribution of the properties \( p, \phi, u \) and \( n_i \) at \( t = 0 \) must be defined as well [13–15].

The bulk equations together with the boundary conditions constitute a well-defined problem where the system responds to the applied driving forces described by boundary conditions on the system’s inlets and outlets. These local boundary conditions can be expressed in terms of conditions on either the potentials \( (\phi, p, n_i) \), or on the fluxes and flows \( (j_i, u) \), or a combination of both. Note that we denoted as a potential any local property whose gradient can drive a fluid or ion flow. Eqs. 2.1-2.9 then describe the electrokinetic responses of the fluidic system in its most general form, including time-dependent and nonlinear effects. We will denote this general description as PNP (Poisson-Nernst-Planck). The nonlinearity originates from the nonlinear couplings in Eqs. 2.2 and 2.5, i.e., when the electrostatic ion distributions are distorted by the fluid flow.

The Gouy-Chapman Model

The Gouy-Chapman model of the electrostatic potential and ion distributions in the diffuse layer follows directly from the PNP equations when considering the
fluidic system to be in thermodynamic equilibrium. For this case, the fluid flow and ion fluxes are zero, \( u = 0 \) and \( j_i = 0 \), and from Eq. 2.5 we find \( \nabla U_i = 0 \). The constant chemical potential corresponds to Boltzmann distributions for the ionic concentrations, \( n_i = n_i^0 \exp \left( -\frac{Z_i e \phi}{kT} \right) \), where \( n_i^0 \) is the concentration of ionic species \( i \) in the bulk. Combining these equilibrium ion concentrations with Poisson’s equation (Eq. 2.3) yields the famous Poisson-Boltzmann relation

\[
\nabla^2 \phi = -\frac{e}{\varepsilon \varepsilon_0} \sum_i Z_i n_i^0 \exp \left( -\frac{Z_i e \phi}{kT} \right)
\]

which is the basis of the Gouy-Chapman model.

**Fluid and Ion Transport between Parallel Plates**

We now derive the equations for a fully developed laminar flow between two charged parallel plates with an applied pressure and potential gradient. This system is depicted in Fig. 2.2 and corresponds to the experimental situation in the Chapters 3-7. The laminar flow and quick development of the steady state situation are ensured by the low Reynolds numbers, \( Re \lesssim 0.01 \), for our experimental conditions [16]. The low Reynolds number indicates that the flow dynamics is dominated by viscous forces, which damp out all turbulences, ensuring a smooth and stable flow. Inertial forces can be neglected, allowing the left hand side of Eq. 2.2 and the effects of gravity to be ignored. The Navier Stokes equation for low \( Re \) then simplifies to Stokes’ equation,

\[
\eta \nabla^2 \mathbf{u} = \nabla p + \rho \nabla \phi.
\]

The linear Stokes relation allows the system to be decoupled into its thermodynamic equilibrium solution in the \( z \)-direction - denoted as subscript “PB” after Poisson-Boltzmann - and into a nonequilibrium solution in the direction of the externally applied driving forces in the \( x \) direction. In thermodynamic equilibrium, all fluxes and flows are zero by definition, and all gradients are zero in the \( x \) and \( y \) direction for symmetry reasons. The externally applied gradients are added to the equilibrium solution, and generate nonzero fluxes. The relations
2.2 Fluid and Ion Transport

between the externally applied driving forces and the resulting fluxes represent the electrokinetic responses of the fluidic system.

We write \( p \) and \( \phi \) as the sum of the external contributions, \( p_{ext} \) and \( \phi_{ext} \), and the thermodynamic equilibrium solution: \( p = p_{ext} + p_{PB} \) and \( \phi = \phi_{ext} + \phi_{PB} \). \( p_{ext} \) and \( \phi_{ext} \) are taken independent of \( y \), yielding the gradients

\[
\nabla p = \frac{\partial p_{ext}}{\partial x} + \frac{\partial p_{PB}}{\partial z} \tag{2.12}
\]

\[
\nabla \phi = \frac{\partial \phi_{ext}}{\partial x} + \frac{\partial \phi_{PB}}{\partial z} \tag{2.13}
\]

Inserting these gradients into Eq. 2.11 while using \( u = u_x \) and \( \nabla^2 u = \frac{\partial^2 u_x}{\partial x^2} \), we find the Stokes’ relations for the fluid transport in the \( x \) and \( z \) directions, respectively:

\[
\eta \frac{\partial^2 u_x}{\partial z^2} = \frac{\partial p_{ext}}{\partial x} + \rho \frac{\partial \phi_{ext}}{\partial x} \tag{2.14}
\]

\[
0 = \frac{\partial p_{PB}}{\partial z} + \rho \frac{\partial \phi_{PB}}{\partial z} \tag{2.15}
\]

Note that the nonzero electrical force on the charges inside the double layer results in a pressure gradient in the \( z \)-direction (Eq. 2.15). The ion flux in the \( x \)-direction is given by the Nernst-Planck equation (Eq. 2.5),

\[
j_{i,x} = -\mu_i n_i \frac{\partial \phi_{ext}}{\partial x} + n_i u_x \tag{2.16}
\]

and the electrical current density \( J_i \) for each ion species is defined as \( J_i = Z_i e j_i \). Eq. 2.14 and 2.16 are the basis for calculating the electrokinetic fluid and ion transport in the \( x \)-direction.

We now solve the equations for the fluid transport and ion transport for a given surface potential (Eq. 2.8) and the no-slip boundary condition (Eq. 2.6). We start with applying a pressure gradient \( \frac{\partial p_{ext}}{\partial x} \) only. The fluid transport equation (Eq. 2.14) then reduces to

\[
\eta \frac{d^2 u_x}{dz^2} = \frac{\partial p_{ext}}{\partial x} \tag{2.17}
\]

Integrating twice yields \( u_x = \frac{1}{8 \eta} \frac{\partial p_{ext}}{\partial x} (4z^2 - h^2) \). Integrating twice yields \( u_x = \frac{1}{8 \eta} \frac{\partial p_{ext}}{\partial x} \), and the integration constants \( C_0 = 0 \) and \( C_1 = -\frac{h^2}{8 \eta} \frac{\partial p_{ext}}{\partial x} \) are solved using the no-slip boundary conditions \( u_x(h/2) = u_x(-h/2) = 0 \). The pressure-driven flow velocity \( u_p \) along the applied gradient between parallel plates is thus given by

\[
u_p = \frac{1}{8 \eta} \frac{\partial p_{ext}}{\partial x} (4z^2 - h^2) \tag{2.17}
\]
The pressure-generated current density $J_p$ follows directly from inserting $\frac{\partial \phi_{\text{ext}}}{\partial x} = 0$ into Eq. 2.16 and summing over all ion species $i$:

$$J_p = \sum_i Z_i e j_{i,x} = \sum_i Z_i e n_i u_p = \rho u_p$$ \hspace{1cm} (2.18)

Applying an electrical field $\frac{\partial \phi_{\text{ext}}}{\partial x}$ only, the Stokes relation for the fluid flow (Eq. 2.14) becomes

$$\frac{\partial^2 u}{\partial z^2} = \frac{\rho}{\eta} \frac{\partial \phi_{\text{ext}}}{\partial x} = -\frac{\varepsilon_0}{\eta} \frac{\partial \phi_{\text{ext}}}{\partial x} \frac{\partial \phi_{PB}}{\partial z}.$$ Integrating twice yields $u_x = -\frac{\varepsilon_0}{\eta} \frac{\partial \phi_{\text{ext}}}{\partial x} \phi_{PB} + C_0 z + C_1$. At the boundaries, $u_x = 0$ and $\phi_{PB} = \zeta$, yielding $C_0 = 0$ and $C_1 = \frac{\varepsilon_0}{\eta} \frac{\partial \phi_{\text{ext}}}{\partial x} \zeta$. The electro-osmotic flow velocity $u_\phi$ is then given by

$$u_\phi = -\frac{\varepsilon_0}{\eta} \frac{\partial \phi_{\text{ext}}}{\partial x} (\phi_{PB} - \zeta)$$ \hspace{1cm} (2.19)

and the field-driven current density $J_\phi$ for $\frac{\partial p_{\text{ext}}}{\partial x} = 0$ is

$$J_\phi = -\frac{\partial \phi_{\text{ext}}}{\partial x} \sum_i Z_i e n_i \mu_i + \rho u_V$$ \hspace{1cm} (2.20)

Because Stokes’ equation is linear, the solutions for the separately applied pressure and potential gradients are additive, $u = u_p + u_\phi$ and $J = J_p + J_\phi$, also when these driving forces would be applied in different directions within the $x-y$ plane.

The macroscopic fluid transport, $Q$, and ionic current, $I$, through a cross-section of the parallel-plates of width $w$ are defined by

$$Q = w \int_{-h/2}^{h/2} (u_p + u_\phi) \, dx$$ \hspace{1cm} (2.21)

$$I = w \int_{-h/2}^{h/2} (J_p + J_\phi) \, dx$$ \hspace{1cm} (2.22)

These expressions accurately model the electrokinetic transport in rectangular channels when $w \gg h$ and $L \gg h$, with $L$ the channel length. We define the linear electrokinetic response properties of a fluidic device as i) the fluidic admittance $\frac{1}{Z_{ch}} = \frac{dQ}{d\Delta p_{\text{ext}}}$, ii) the streaming conductance $S_{str} = \frac{dI}{d\Delta p_{\text{ext}}}$, iii) the electro-osmotic fluidic admittance $\frac{dQ}{d\Delta \phi_{\text{ext}}}$, and iv) the electrical conductance $\frac{1}{R_{ch}} = \frac{dI}{d\Delta \phi_{\text{ext}}}$. These measurable device properties relate the macroscopic fluidic and ionic transport to the applied pressure and potential differences, and are in general not limited to a particular device geometry, electrical surface condition, or salt concentration.
The Poisson-Boltzmann Solution between Parallel Plates

To numerically evaluate the electrokinetic responses of our slit-like nanochannels, we must solve the potential and charge distributions using the Poisson-Boltzmann equation. We consider the case of a symmetrical salt with concentration $n$, where the positive and negative ions are of opposite valence, $Z$ and $-Z$. The Poisson-Boltzmann equation (Eq. 2.10) then reduces to

$$\frac{\partial^2 \psi_{PB}(z)}{\partial z^2} = \kappa^2 \sinh (\psi_{PB}(z))$$  \hspace{1cm} (2.23)

for the $z$-direction, where $\psi_{PB}(z) = \frac{Ze}{kT} \phi_{PB}(z)$ is the dimensionless potential, $1/\kappa$ the Debye screening length, defined by $\kappa^2 = \frac{2Ze^2n}{\epsilon\epsilon_0 kT}$. For equal, negatively-charged surfaces ($\zeta < 0$ or $\sigma < 0$) [17], the analytical solution for the dimensionless potentials given by [12, 18]

$$\psi_{PB}(z) = \psi_{PB}(0) + 2 \ln \left[ \text{JacCD} \left( \frac{KZ}{2} e^{-\psi_{PB}(0)/2} \right) \right] \ \zeta, \sigma < 0 \hspace{1cm} (2.24)$$

where $\psi_{PB}(0)$ is the potential in the center between the parallel plates and JacCD($l|m$) is the Jacobian elliptic function with argument $l$ and parameter $m$. $\psi_{PB}(0)$ is solved for the electrical boundary condition, $\zeta$ (Eq. 2.8) or $\sigma$ (Eq. 2.9), at $z = h/2$. Unfortunately, $\psi_{PB}(0)$ cannot be expressed by a simple function of $h$, $\kappa$, and $\zeta$ or $\sigma$, and must be evaluated numerically. The potential between positively charged surfaces is solved using $\psi_{PB}(z)|_{\zeta, \sigma > 0} = -\psi_{PB}(z)|_{-\zeta, -\sigma}$. For more complex situations, such as oppositely charged surfaces and asymmetrical salts (which was the case in Chapter 4), no analytical solutions are available, and the Poisson-Boltzmann equation must be solved numerically [19].

The behavior of $\psi_{PB}(z)$, given by Eq. 2.24, is considered for several limiting cases. For weakly-overlapping double layers ($k\kappa \gg 1$), the potential is almost zero in the center of the channel and both surfaces can be treated separately. The analytical solution for the double layer adjacent to a single flat surface can be found in literature [20], which reduces for low $\zeta$ to the familiar exponential decay of $\psi_{PB}(z)$. For strong double layer overlap ($k\kappa \ll 1$), co-ions are expelled from the solution, and Eq. 2.24 reduces to $\psi_{PB}(z) = \psi_{PB}(0) + 2 \ln \left[ \cos \left( \frac{KZ}{2} e^{-\psi_{PB}(0)/2} \right) \right]$. The derivation of this expression is given in Chapter 5.8 of this thesis. For this case of strong overlap, $\psi_{PB}(z)$ is found to be relatively constant across the channel height when $\sigma h$ is small, leading to a relatively homogeneous counterion distribution. For large $\sigma h$, the counterion concentration strongly peaks close to the charged walls. These effects lead to an optimal $\sigma h$ when the slit-like nanochannel is evaluated in terms of its electrokinetic energy conversion ability, where hydrostatic energy is converted into electrical energy (see Chapter 5).
2.3 Charge Inversion

Charge inversion is the counterintuitive phenomenon, where the effective surface charge of a highly charged surface changes sign due to the strong accumulation of multivalent counterions (Z-ions) at the surface. Charge inversion has been observed in experiments [21–24], and is predicted by numerical simulations [25–27] and analytical ion correlation models [28–31] where the discrete nature of charge is accounted for. Mean-field theories, such as Poisson-Boltzmann theory, do not predict charge inversion. Ion correlation theory has been successful in describing experiments for \( Z \geq 3 \), both with and without additional screening by monovalent salt (Chapter 4, [23]). We will describe the basic picture that underlies this theory, and discuss the corresponding equations and their predictions of charge inversion for weak and strong screening in a liquid.

Ion Correlation Theory

Due to strong interactions with the highly charged surface and with each other, screening Z-ions do not position themselves randomly in three-dimensional space, but form a strongly correlated liquid on the surface. The short-range ordering of this liquid is reminiscent of a Wigner crystal, see Fig. 2.3. The strong attraction to the surface confines the Z-ions into a two-dimensional-like sheath, and the strong repulsion between the ions maximizes their distance and explains the hexagonal ordering. The ions each have a radius of \( r_{ion} \) and a charge of \( Ze \). We define the effective surface charge density \( \sigma^* = \sigma_b + nZe \), where \( \sigma_b \) is the bare silica charge density and \( n \) the number density of the Z-ions at the surface. The Z-ions are assumed to be located in the Stern layer behind the no-slip plane, and as a result \( \sigma^* \) is the electrical boundary condition for the diffuse layer. Ion correlation theory assumes that the Z-ions at the surface are in thermodynamic equilibrium with those in the bulk,

\[
\Delta \mu = \mu_c + kT \ln \left( \frac{n}{2c r_{ion}} \right) + \Delta \mu^0 = 0,
\]

(2.25)

where \( \Delta \mu \) is the difference in chemical potential between surface and bulk Z-ions, \( \mu_c \) is the chemical potential associated with the correlations and the electrostatic potential, \( kT \ln \left( \frac{n}{2c r_{ion}} \right) \) represents the entropy of mixing, and \( \Delta \mu^0 \) accounts for specific adsorption and hydration effects. The entropy of mixing accounts for the difference between the Z-ion concentration in the bulk, \( c \), and the Z-ion concentration at the surface, \( n/2r_{ion} \).
2.3 Charge Inversion

![Figure 2.3](image)

**Figure 2.3:** a) Strongly correlated liquid of $Z$-ions on an oppositely charged surface. The ions in the diffuse layer further away from the surface are predominantly co-ions when charge-inversion occurs. b) Top view of the hexagonal pattern of the Wigner crystal, which depicts the ordering of multivalent counterions of charge $Ze$ and radius $r_{ion}$ adjacent to a charged surface.

**Multivalent Ions with no Added Salt**

Charge inversion occurs already at very low concentrations of multivalent ions, namely at $100 - 300 \mu M$ for $Z = 3$ and at $\sim 10 \mu M$ for $Z = 4$ [22, 23]. Due to the low salt concentrations in typical experiments, the Debye screening length is long and screening between the correlated ions at the surface may be considered weak. For the case of weak screening and neutral systems, $\sigma^* = 0$, the correlation energy is well approximated by calculations for two-dimensional electron liquids, embedded in a neutralizing background [32–34]. An important parameter for these systems is the Coulomb coupling constant, $\Gamma = \frac{\sqrt{\sigma_b Z^3 e^3}}{4 kT \epsilon \epsilon_0}$, which represents the correlation energy per $Z$-ion relative to $kT$. For a typical surface charge $\sigma_b = -0.15 \text{ C/m}^2$, we obtain $\Gamma = 1.2, 3.5, 6.4$ and $9.8$ for $Z = 1, 2, 3$ and $4$, respectively. Short-range ion correlations are important when $\Gamma \gg 1$, and the long-range hexagonal ordering of the Wigner crystal occurs when $\Gamma \gtrsim 130$ [35]. The correlation energy for short- and long-range ordering is quite similar, as the interactions are strongest with nearby $Z$-ions. The chemical potential for $\Gamma \leq 50$ was calculated to be [29, 34]

$$\mu_{WC} = -kT \left( 1.65\Gamma - 2.61\Gamma^{1/4} + 0.26 \ln \Gamma + 1.95 \right). \quad (2.26)$$

Note that this expression was calculated for a neutral system, where the average electrostatic potential of the surface is zero. Away from neutrality, $\sigma^* \neq 0$, an electrostatic contribution must be added to the correlation energy [28], yielding

$$\mu_c = \mu_{WC} + Ze \phi_s \quad (2.27)$$

where $\phi_s$ is the average surface potential. Inserting the condition $\sigma^* = 0$ (and
therefore $\phi_s = 0$) into Eq. 2.25 yields an expression for the charge inversion concentration,

$$c_0 = \left| \frac{\sigma_b}{2r_{ion}Ze} \right| \exp \left( \frac{\mu_c}{kT} \right) \exp \left( \frac{\Delta \mu^0}{kT} \right),$$  \hspace{1cm} (2.28)

which represents the bulk Z-ion concentration for which the surface is exactly neutral. At higher bulk concentrations, $c > c_0$, the surface will be charge inverted, while for smaller bulk concentrations, $c < c_0$, the effective surface charge will be of the same sign as $\sigma_b$. Predictions of $c_0$ by Eq. 2.28 corresponded excellently to surface force measurements for $Z = 3$ and $Z = 4$ [23], confirming the validity of this model for weak screening and neutral surfaces.

Mixtures of Multivalent and Monovalent Ions

When additional monovalent salt is added to the multivalent ions in the solution, the electrostatic interactions in the correlated liquid will be strongly affected by screening. For this case, the energy gain due to the Wigner crystal formation is no longer accurately represented by Eq. 2.26, which was calculated for systems where the correlated point-charges lie in-plane with a homogeneous background charge in the absence of screening. The finite distance, $d$, between the Z-ions and the surface in real systems will significantly affect the electrostatic environment of the Z-ions in the presence of strong screening. The equilibrium amount of condensed Z-ions for this case can be obtained by calculating the free energy, $F$, explicitly by summing over all charges in the presence of screening, and then minimizing $F$. In this approach, the monovalent salt is only represented through its effect on the screening length, $1/\kappa$.

We calculate the free energy $F$ stored in the distribution of the free charges, $\rho_f$, in the presence of a dielectric wall. $\rho_f$ consists of the Z-ions of charge $Ze$ and the bare surface charge $\sigma_b$, but does not include the polarization charge, $\sigma_{bnd}$ induced by the dielectricum (see Fig. 2.4a). This situation corresponds to our experiments in Chapter 4. $F$ is defined as [36]

$$F = \frac{1}{2} \int_v \rho_f \phi dv,$$  \hspace{1cm} (2.29)

where $\phi$ is the electrostatic potential and $v$ the volume for which the free energy $F$ is calculated. Note that the polarization charge, $\sigma_{bnd}$, is not included in the integral, but still affects $F$ as it changes the potential.

The image charges as shown in Fig. 2.4b have exactly the same effect on the potential in the electrolyte as the dielectric wall in Fig. 2.4a, and the free energy
is the same for both situations. The multiplication factor, $f_{im} = \frac{\epsilon_1 - \epsilon_2}{\epsilon_1 + \epsilon_2}$, defines the ratio of the magnitude of the image charges to the free charges. In the absence of a dielectric wall ($\epsilon_1 = \epsilon_2$), we obtain $f_{im} = 0$ as there are no polarization charges. For $\epsilon_2 = 0$, we find $f_{im} = 1$ and the image charges are equal in magnitude to the free charges. For this case, all field lines are expelled from the device material. This is close to our experimental conditions, where $\epsilon_1 \approx 80$, $\epsilon_2 \approx 4$, and $f_{im} \gtrsim 0.9$.

Replacing the dielectric (Fig. 2.4a) with image charges (Fig. 2.4b) simplifies the calculation of the free energy. The potential at distance $r$ from a point charge $q_j$ in a screening environment using the Debye-Hückel approximation is defined as $\phi_j(r) = \frac{q_j}{4\pi\epsilon_0 r} e^{-\kappa r}$ [19]. The contribution to $F$ of each free point charge $q_i$ due to the potential emanating from $q_j$ is then $F_{ij} = \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} e^{-\kappa r_{ij}}$, and the total free energy is given by

$$F = \sum_i \sum_{j>i} F_{ij} = \frac{1}{2} \sum_i \sum_{j\neq i} F_{ij} = \frac{1}{2} \sum_{k=1}^{4} Q_k \sum_{m=1}^{4} \phi_m,$$

where $Q_k = \sum_i q_i$ is the sum of the charges in group (k), $\phi_m = \frac{1}{4\pi\epsilon_0} \sum_{j\neq i}^m \frac{q_i q_j}{r_{ij}} e^{-\kappa r_{ij}}$ is the potential due to the charges in group (m), and (1), (2), (3) and (4) denote
groups of charges containing $\sigma_0$, $Ze$, $f_{im}\sigma_b$ and $f_{im}Ze$, respectively (see Fig. 2.4b). $Q_k$ of an area $A$ is easily calculated for each group of charges as $Q_1 = \sigma_b A$ and $Q_2 = ZenA$. $\phi_1$ is obtained by integrating $\sigma_b$ over the infinite plane. For symmetry reasons, $\phi_1$ can only be a function of $d$, and we split $r_{ij}$ into its orthogonal components, $d$ and $x_{ij}$, where $x_{ij}$ is in the direction parallel to the surface. Using the substitutions $x_{ij} = \sqrt{r_{ij}^2 - d^2}$ and $\frac{dx_{ij}}{dr_{ij}} = \frac{r_{ij}}{\sqrt{r_{ij}^2 - d^2}}$, we calculate

$$
\phi_1(d) = \frac{1}{4\pi\epsilon\epsilon_0} \int_{r_{ij}} dq_{ij} e^{-\kappa r_{ij}} = \frac{1}{4\pi\epsilon\epsilon_0} \int_0^\infty \frac{2\pi x_{ij} \sigma_b}{r_{ij}} e^{-\kappa r_{ij}} dx_{ij}
$$

$$
= \frac{1}{2\epsilon\epsilon_0} \int_d \sqrt{r_{ij}^2 - d^2} \sigma_b e^{-\kappa r_{ij}} r_{ij} \sqrt{r_{ij}^2 - d^2} dr_{ij}
$$

$$
= \frac{\sigma_b}{2\epsilon\epsilon_0} \left( -\frac{1}{\kappa} e^{-\kappa d} \right) \bigg|_d = \frac{\sigma_b}{2\epsilon\epsilon_0\kappa} e^{-\kappa d}
$$

(2.31)

and $\phi_3(d) = f_{im}\phi_1(d)$. Eq. 2.31 is the familiar result of the exponentially decreasing potential predicted by the Debye-Hückel approximation [19]. Note also that the familiar Grahame equation for the $\zeta$-potential is recovered when the field is completely expelled from the dielectric material ($f_{im} = 1$): $\zeta = \phi_1(0) + \phi_3(0) = \frac{\sigma_b}{\epsilon\epsilon_0\kappa}$. The expressions for $\phi_2$ and $\phi_4$ cannot be simplified and will be evaluated numerically. The contributions to the free energy, $F_{km} = \frac{1}{2} Q_k \phi_m$, are given by

$$
F_{11} = \frac{1}{2} Q_1 \phi_1(0) = \frac{\sigma_b^2 A}{4\epsilon\epsilon_0\kappa},
$$

(2.32)

$$
F_{21} = \frac{1}{2} Q_2 \phi_1(d) = \frac{\sigma_b ZenA}{4\epsilon\epsilon_0\kappa} e^{-\kappa d},
$$

(2.33)

$$
F_{22} = \frac{1}{2} Q_2 \frac{1}{4\pi\epsilon\epsilon_0} \sum_{j\neq i}^{(2)} \frac{q_j}{r_{ij}^2} e^{-\kappa r_{ij}} = \frac{ZenA}{8\pi\epsilon\epsilon_0} \frac{Ze}{r_j} \sum_{r_j \neq 0} e^{-\kappa r_{ij}},
$$

(2.34)

$$
F_{24} = \frac{1}{2} Q_2 \frac{1}{4\pi\epsilon\epsilon_0} \sum_{j\neq i}^{(4)} \frac{q_j}{r_{ij}^2} e^{-\kappa r_{ij}} = \frac{ZenA}{8\pi\epsilon\epsilon_0} \frac{f_{im}Ze}{r_j} \sum_{r_j} e^{-\kappa \sqrt{r_j^2 + (2d)^2}},
$$

(2.35)

$F_{12} = F_{21}$, $F_{13} = f_{im}F_{11}$ and $F_{14} = F_{23} = f_{im}F_{21}$, where $r_j$ are the lattice vectors of the two-dimensional Wigner crystal. The total free energy of the system is
2.3 Charge Inversion

given by the sum of all contributions,

\[ F = (1 + f_{im})F_{11} + (2 + 2f_{im})F_{21} + F_{22} + F_{24} = \]

\[ \frac{A\sigma_b^2}{2\epsilon\epsilon_0\kappa} + \frac{A\sigma_b nZe e^{-\kappa d}}{\epsilon_0\kappa} + \frac{AnZ^2e^2}{8\pi\epsilon\epsilon_0} \sum_{r_j\neq0} \frac{e^{-\kappa r_j}}{r_j} + \frac{AnZ^2e^2}{8\pi\epsilon\epsilon_0} \sum_{r_j} \frac{e^{-\kappa\sqrt{r_j^2 + 4d^2}}}{\sqrt{r_j^2 + 4d^2}} \]  

(2.36)

for \( f_{im} = 1 \), which is the expression that was proposed by several theoretical papers [30, 31] and used in Chapter 4. The first term represents the self energy of the bare surface charge and its equal image charge, the second term represents the attractive interaction between the bare surface charge and the Z-ions, the third term accounts for the repulsion between the Z-ions in the Wigner crystal plane, and the fourth term accounts for the repulsion between the Z-ions and their image charges [31]. The summations that underlie Eq. 2.36 assume long-range hexagonal ordering of the Wigner crystal, while only short-range ordering occurs for real experimental conditions (5 \( \lesssim \Gamma \lesssim 15 \)). However, the correlation energy for short-range ordering is similar to that of long-range ordering (\( \sim 11\% \) difference for \( \Gamma = 5 \)) [29], and Eq. 2.36 may be applied to good approximation.

The equilibrium density of multivalent ions at the surface in the presence of screening is found calculating the chemical potential through \( \mu_c = \partial F/\partial (nA) = \partial (F/A)/\partial n \) and solving \( \Delta \mu = 0 \) using Eq. 2.25. We also minimize \( F \) with respect to the separation between the Z-ions and the surface by solving \( \partial F/\partial d = 0 \), while imposing \( d \geq r_{ion} \). When the entropy of mixing and specific adsorption effects are ignored, a strong enhancement of charge inversion as function of salt concentration is predicted [31]. In contrast, including \( kT \ln \left( \frac{n}{2\pi r_{ion}} \right) \) and \( \Delta \mu^0 \) can lead to a reduction of charge inversion, depending on the numerical value of \( \Delta \mu_0 \). Our experiments in Chapter 4 correspond well this latter model, and reveal a reduction of charge inversion as function of salt concentration. At very high monovalent salt concentrations, the experimental results deviated from the model predictions, and Z-ions were seen to have no effect on \( \sigma^* \) any longer. This points to the breakdown of ion correlations as an important factor in the chemical potential balance at high monovalent salt concentrations, which could be due to i) the reduced Coulomb interactions (\( \Gamma \)) due to screening, ii) a lower effective ion valence due to the pairing of monovalent and multivalent ions, and iii) screening of \( \sigma_b \) by monovalent ions through a competition for charged sites.
2.4 DNA Polymers in Confinement

This section describes the main theoretical models regarding the distribution of polymers between parallel plates [37–39]. Flexible polymers can take up an enormous number of configurations by the rotation about chemical bonds. The shape of the polymers can therefore only be usefully described statistically. We first describe the ideal polymer, whose conformations are governed by a random walk of segments with a fixed length \( b \) (Fig. 2.5). We derive the segment distribution for an unconfined molecule, and subsequently present expressions for an ideal polymer confined between parallel plates. At the end of this section we present the theory for non-ideal polymers, which takes the excluded volume effect into account. These models are compared with our experiments on DNA transport in confinement (Chapter 7).

The Freely Jointed Chain

The freely jointed chain model assumes a chain of \( N \) connected segments with fixed length \( b \), each pointing into a random direction (Fig. 2.5). The conformation of the freely jointed chain is represented by the position vectors of the joints, \( R_n = R_0 \ldots R_N \), or alternatively by the segment vectors, \( r_n = r_1 \ldots r_N \), where

\[
  r_n = R_n - R_{n-1}, \quad n = 1, 2, \ldots, N. \tag{2.37}
\]

The end-to-end vector of the polymer conformation is defined as [40]

\[
  R = R_N - R_0 = \sum_{n=1}^{N} r_n. \tag{2.38}
\]

The normalized probability distribution of each segment \( r_n \) is given by

\[
  \varphi(r) = \frac{1}{4\pi b^2} \delta(|r| - b), \tag{2.39}
\]

and the probability for a given conformation \( \{r_n\} \) is written as

\[
  \Psi(\{r_n\}) = \prod_{n=1}^{N} \varphi(r_n). \tag{2.40}
\]
Let $\Phi(R, N)$ be the probability distribution function that a chain consisting of $N$ links has end-to-end vector $R$. Integrating over all possible conformations yields

$$
\Phi(R, N) = \int dr_1 \int dr_2 \cdots \int dr_N \delta\left( R - \sum_{n=1}^{N} r_n \right) \Psi(\{ r_n \}) \tag{2.41}
$$

where the Dirac delta function $\delta(r)$ can be written as $\delta(r) = \frac{1}{(2\pi)^3} \int_{-\infty}^{+\infty} e^{ikr} dk [41]$. Rewriting Eq. 2.41 and using $e^{ik\left( R - \sum_{n=1}^{N} r_n \right)} = e^{ikR} \prod_{n=1}^{N} e^{-ikr_n}$ yields

$$
\Phi(R, N) = \frac{1}{(2\pi)^3} \int dk e^{ikR} \int dr_1 \cdots dr_N \prod_{n=1}^{N} e^{-ikr_n} \varphi(r_n) = \frac{1}{(2\pi)^3} \int dk e^{ikR} \left[ \int dr e^{-ikr} \varphi(r) \right]^N \tag{2.42}
$$

Evaluating the integral over $r$ using polar coordinates yields

$$
\int dr e^{-ikr} \varphi(r) = \frac{1}{4\pi b^2} \int_0^{2\pi} d\theta \int_0^\infty dr \sin(\theta) e^{-ikr \cos \theta} \delta(r - b) = \frac{\sin(kb)}{kb} \tag{2.43}
$$

with $k = |k|$ and $r = |r|$, leading to the well-known Gaussian distribution for the end-to-end vector [42],

$$
\Phi(R, N) = \frac{1}{(2\pi)^3} \int dk e^{ikR} \left( \frac{\sin(kb)}{kb} \right)^N \approx \frac{1}{(2\pi)^3} \int_{-\infty}^{+\infty} dk e^{ikR} \exp\left( -\frac{Nk^2b^2}{6} \right) \quad N \gg 1, \; |R| \ll Nb
$$

$$
= \left( \frac{3}{2\pi Nb^2} \right)^{3/2} \exp\left( -\frac{3R^2}{2Nb^2} \right). \tag{2.44}
$$

The Gaussian distribution of Eq. 2.44 is valid for large molecules ($N \gg 1$) that are far from being fully stretched ($|R| \ll Nb$). Approximations with a wider range of validity are presented in literature [37, 38], but the Gaussian probability distribution is sufficiently accurate for even the shortest molecule that we studied experimentally (Chapter 7): For $N = 40$ and $b = 100$ nm we find $< 0.5\%$ error for $\Phi(R, N)$ in the range $|R| \leq 0.2Nb$. For larger $|R|$, the relative error grows but the probability of finding a segment becomes vanishingly small.
Chapter 2: Theoretical Concepts

Confinement between Parallel Plates

The easiest way to solve the probability distribution of the freely jointed chain in confinement is through the use of a diffusion equation [37, 43]. This method is valid, because diffusion is also a random walk process. The diffusion equation is accurate for a sufficiently large concentration of randomly-walking particles, which corresponds to the center area \(|R| \ll Nb\) of a large polymer \((N \gg 1)\). The presence of a hard wall is easily modeled by taking the segment concentration zero at the boundaries, and solving the diffusion equation in the volume containing the polymer. This route is equivalent to solving this problem using Green functions, as treated by Doi et al. [39].

The diffusion equation for the polymer segments is given by [37]

\[
\frac{\partial \Phi(R, N)}{\partial N} = \frac{b^2}{6} \nabla^2 \Phi(R, N). \tag{2.45}
\]

Note that the Gaussian distribution of Eq. 2.44 is a solution to this differential equation, which confirms that the statistical approach is equivalent to using the diffusion equation. The segment probability at the positions of the parallel plates at \(z = 0\) and \(z = h\) (see Fig. 2.6) is taken zero: \(\Phi(z, N)|_{z=0} = \Phi(z, N)|_{z=h} = 0\). Solving Eq. 2.45 for the \(z\)-direction with these boundary conditions yields the probability of finding a polymer starting at \(z'\) and ending at \(z\) [39]:

\[
\Phi_z(z|z', N) = \frac{2}{h} \sum_{p=1}^{\infty} \sin \left( \frac{p\pi z}{h} \right) \sin \left( \frac{p\pi z'}{h} \right) \exp \left( -\frac{p^2\pi^2 Nb^2}{6h^2} \right). \tag{2.46}
\]

The distribution in the unconfined \(x - y\) direction is given by the Gaussian distribution \(\Phi_{xy}(x, y|[0, 0], N) = \frac{3}{2\pi Nb^2} \exp \left( -\frac{3(x^2+y^2)}{2Nb^2} \right) [42]\) for a polymer starting at \(x = y = 0\). The probability density in three dimensions is then given by \(\Phi([x, y, z]|[0, 0, z'], N) \propto \Phi_{xy}([x, y|[0, 0], N)\Phi_z(z|z', N) [44]\). This expression represents the unnormalized probability density for finding an unrestricted chain of \(N\) steps which starts at \([0, 0, z']\) and ends at \([x, y, z]\), and which is located entirely inside the slab. Integration over \(x, y\) and \(z\) gives the probability that a random

\[\text{Figure 2.6: A polymer is confined in the } z\text{-direction between parallel plates at } z = 0 \text{ and } z = h. \text{ The probability of finding both parts of a freely jointed chain (}N\text{ and }L/b - N\text{ steps) completely between the parallel plates defines the segment concentration density (eqs. 2.47-2.48).}\]
2.4 DNA Polymers in Confinement

Flight beginning at height \( z' \) remains inside the slab:

\[
P(z', N) \propto \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{z=0}^{h} \Phi(x, y, z|0, 0, z', N) dx dy dz \tag{2.47}
\]

\[
= \frac{4}{\pi} \sum_{m=0}^{\infty} \frac{1}{2m+1} \exp \left( -\frac{(2m+1)^2 \pi^2 Nb^2}{6h^2} \right) \sin \left( \frac{\pi z'(2m+1)}{h} \right).
\]

The asymmetry in the \( z \)-direction causes the probability to depend on the starting position \( z' \) of the polymer. The probability of finding the \( N \)th segment of a polymer of length \( L \) at position \( z' \) is given by \( P(z', N)P(z', \frac{L}{b} - N) \), as illustrated in Fig. 2.6. Integrating over all \( N \) yields the segment concentration distribution,

\[
\rho(z') \propto \int_{0}^{L/b} P(z', N)P(z', \frac{L}{b} - N) dN. \tag{2.48}
\]

Useful approximations for \( \rho(z') \) exist for the regimes of strong confinement and for no confinement at all. We take the radius of gyration, \( R_g = \sqrt{\frac{Nb^2}{6}} \) [40], as the typical size of an unconfined polymer. For strong confinement, \( h \ll R_g \), the exponential in Eq. 2.47 quickly drops to zero for higher orders of \( m \). The \( m = 0 \) term of this equation is found to be an excellent approximation for the regime \( h < R_g \), leading to a segment concentration of

\[
\rho(z') \propto \sin^2 \left( \frac{\pi z'}{h} \right), \quad h < R_g. \tag{2.49}
\]

Interestingly, the segment density is not a function of the polymer size in this regime of strong confinement.

In the absence of confinement, \( h > 10R_g \), the probability distribution becomes homogeneous in the center, and the segment density is very well approximated by the density profile adjacent to a single surface [45], \( \rho(z') \propto \tanh^2 \left( \frac{\sqrt{\pi} z'}{2R_g} \right) \). For two surfaces, we write

\[
\rho(z') \propto \tanh^2 \left( \frac{\sqrt{\pi}}{2R_g} \left( \left| z' - \frac{h}{2} \right| - \frac{h}{2} \right) \right), \quad h > 10R_g. \tag{2.50}
\]

The distribution of segments in the \( z \)-direction is used to calculate the center-of-mass polymer velocity, \( \overline{u} \), as the average velocity of the segments. Assuming that each segment travels at the local fluid speed \( u(z') \), we find

\[
\overline{u} = \int_{0}^{h} \rho(z')u(z') dz' / \int_{0}^{h} \rho(z')dz'. \tag{2.51}
\]

This result was successfully applied to model experimental values for \( \overline{u} \) as function of \( h \) for various DNA lengths in Chapter 7.
The Non-ideal Polymer in Confinement

Models for non-ideal polymers account for the fact that a polymer does not occupy the same space twice. This excluded volume effect is ignored in the freely jointed chain model, and causes an increase of the molecule’s size. In this section, we present scaling relations for the size and the self diffusion constant of the non-ideal polymer in confinement.

Flory [46] modeled the excluded volume effect as a self-avoiding random walk, and found a polymer radius of \( R \propto N^{\nu} \), where \( \nu = 3/5 \) for a self-avoiding walk in three dimensions, and \( \nu = 3/4 \) for two dimensions. Upon confinement, the non-ideal polymer organizes into a chain of smaller ‘blobs’ [47, 48], whose radius is proportional to the slit height, \( R_{\text{blob}} \propto h \) (Fig. 2.7a). The polymer behavior inside the blobs is considered to be three-dimensional in nature, and we may write \( R_{\text{blob}} \propto N_{\text{blob}}^{3/5} \), where \( N_{\text{blob}} \) is the number of segments in each blob. The number of blobs, \( N \), is then given by

\[
N = \frac{N}{N_{\text{blob}}} = \left( \frac{R_{g}}{R_{\text{blob}}} \right)^{5/3} \propto \left( \frac{R_{g}}{h} \right)^{5/3}.
\]

The blobs themselves exhibit a two-dimensional self-avoiding random walk with step size \( h \) (Fig. 2.7b), resulting in a radius in the unconfined direction of \( R_{xy} = h N^{3/4} \propto h \left( \frac{R_{g}}{h} \right)^{5/4} \), or \( R_{xy} \propto \left( \frac{R_{g}}{h} \right)^{1/4} \). The diffusion constant \( D \) scales as \( D \propto 1/\xi \propto 1/R \), with \( \xi \) the drag of a polymer chain of three-dimensional radius \( R \). In a slit, hydrodynamic interactions are strongly screened over length scales larger than \( h \), and the drag on the polymer may be taken as the sum of the individual blobs. We write \( D_{xy} \propto 1/N R_{\text{blob}} \), leading to the scaling relation

\[
\frac{D_{xy}}{D_{\text{bulk}}} = \frac{R_{g}}{R_{\text{blob}}} \propto \frac{R_{g}}{h} \left( \frac{R_{g}}{h} \right)^{-5/3} = \left( \frac{R_{g}}{h} \right)^{-2/3} \quad (2.52)
\]

This scaling of the diffusion constant is consistent with molecular dynamics simulations [49] and with our experiments in Chapter 7.

\[\text{Figure 2.7: a) A self-avoiding polymer chain forms blobs of diameter } 2R_{\text{blob}} \approx h \text{ when confined between parallel plates. Inside the blobs, the polymer behavior is three-dimensional in nature. (b) Top view. The blobs exhibit a two-dimensional self-avoiding walk between the parallel plates.}\]
2.5 Taylor Dispersion in a Slit-like Geometry

This last section of the theory chapter treats the dispersion of point-like particles in a pressure-driven flow. We will derive the dispersion relation for the parallel plate geometry, analogous to Taylor’s treatment for a capillary [50]. For the rectangular geometry in our experiments (Chapter 7), a correction to the parallel plate solution is needed, which is presented at the end of this section.

A narrow plug of a substance of concentration \( c \) disperses in a pressure-driven flow due to the strong \( z \)-dependence of the fluid velocity \( u(z) \) (Fig. 2.8a). Taylor assumed that transport of the substance is dominated by convection in the \( x \)-direction, and by diffusion in the \( z \)-direction [50]. The transport can therefore be visualized as a series of consecutive steps of convection and diffusion as illustrated in Fig. 2.8b, whose combined effect lead to Taylor dispersion. For the no-slip boundary condition at the channel walls, \( u(h/2) = u(-h/2) = 0 \), the pressure driven fluid velocity is given by \( u(z) = \frac{\Sigma p}{8\eta} (h^2 - 4z^2) \) with \( \nabla p \) the applied pressure gradient and \( \eta \) the fluid viscosity. We define a reference plane which moves with the mean speed of the flow, \( u_{av} = \frac{\Sigma p}{8\eta} \), and \( u_{av} x \) moves with this plane, and the fluid velocity relative to this plane is \( u'(z) = \frac{\Sigma p}{8\eta} (h^2 - 4z^2 - \frac{2}{3}h^2) = \frac{\Sigma p}{32\eta} (h^2 - 12z^2) \). Material that is convectively transported across the reference plane is assumed to diffuse away in the \( z \) direction. Neglecting diffusion in the \( x \)-direction, conservation of mass then yields

\[
D \frac{\partial^2 c}{\partial z^2} = \frac{\partial c}{\partial x'} u'(z) = \frac{\partial c}{\partial x'} \frac{\nabla p}{24\eta} (h^2 - 12z^2) \tag{2.53}
\]

A solution for \( c \) is found by substituting \( c = c_{x'} + \alpha_1 z^2 + \alpha_2 z^4 \) into Eq. 2.53, where \( c_{x'} \) only depends on \( x' \). We find \( D \frac{\partial^2 c}{\partial x'^2} = D(2\alpha_1 + 12z^2 \alpha_2) = \frac{\partial c}{\partial x'} \frac{\nabla p}{24\eta} (h^2 - 12z^2) \), which solves the constants \( \alpha_1 = \frac{\partial c}{\partial x'} \frac{\nabla p}{48\eta D} \) and \( \alpha_2 = -\frac{\partial c}{\partial x'} \frac{\nabla p}{24\eta D} \), yielding

\[
c = c_{x'} + \frac{\partial c}{\partial x'} \frac{\nabla p h^2}{48\eta D} z^2 - \frac{\partial c}{\partial x'} \frac{\nabla p}{24\eta D} z^4 \tag{2.54}
\]

Taylor assumed that diffusion is sufficiently fast to keep variations in the \( z \)-direction much smaller than those in the \( x \)-direction. This allows us to write \( \partial c/\partial x' \approx \partial c_m/\partial x' \) with \( c_m \) the mean concentration across the channel height. The total amount of substance that is transported per unit time across the reference plane of width \( w \) can then be written as

\[
Q_c = w \int_{-h/2}^{h/2} u'(z) c \, dz = -\frac{\nabla p^2 wh^7}{30240\eta^2 D} \frac{\partial c_m}{\partial x'} \tag{2.55}
\]
Chapter 2: Theoretical Concepts

**Figure 2.8:** a) Taylor dispersion in a slit-like channel. A substance of concentration \( c \), introduced into the channel as a narrow plug at \( t = 0 \) and \( x = 0 \), is dispersed in a pressure-driven flow to a much broader distribution after a certain time. The substance will be convectively transported across a reference plane (dashed line) moving with the average speed of the flow. Diffusion will act to keep the concentration homogeneously distributed in the \( z \)-direction. b) Taylor dispersion can be understood intuitively as a number of successive steps, whereby the substance is alternatingly convectively transported in the \( x \)-direction and diffusively transported in the \( z \)-direction.

Conservation of mass dictates that a net transport across the reference plane must lead to a change of the mean concentration, which is expressed through the relation \(- \frac{1}{wh} \frac{\partial Q}{\partial x'} = \frac{\partial c_m}{\partial t}\). Rewriting using Eq. 2.55 yields the diffusion equation

\[
\frac{k}{h^2} \frac{\partial^2 c_m}{\partial x'^2} = \frac{\partial c_m}{\partial t} \quad (2.56)
\]

with the Taylor diffusion constant

\[
k = \frac{\nabla p^2 h^6}{30240 \eta^2 D} = \frac{h^2 u_{av}^2}{210 D} \quad (2.57)
\]

This result is also recovered from expressions for open chromatographic channels if we ignore the stationary phase [51, 52], which corresponds to our experimental conditions.

In the original paper by Taylor [50], the above derivation was done for the capillary geometry, yielding a diffusion constant of \( k = \frac{h^2 u_{av}^2}{192 D} \). This \( k \) is nearly identical to our result for a slit-like channel, Eq. 2.57. The result for rectangular channels turns out to be quite different [52–55], even for channels with high aspect
ratios where the parallel plate solution would be intuitively expected. The reason for this is the lower fluid speed close to the side walls, which causes the substance to lag behind there. Diffusion eventually distributes the substance across the full channel width, leading to enhanced dispersion everywhere in the rectangular geometry. From this qualitative picture, it can be readily understood that the dispersive properties of a rectangular channel depend on the experimental timescale, $\tau_{exp}$, relative to the typical diffusion times in each direction $[53, 55]$.

When the observation time is short compared to the typical diffusion time across the channel height, $\tau_{exp} \leq \tau_h = \frac{0.5h^2}{D}$, only convectional dispersion occurs. This case corresponds to the first step in Fig. 2.8b and was theoretically worked out by Taylor $[50]$. For intermediate observation times, the dispersion gradually shift from the parallel plate situation (Eq. 2.57) for $\tau_h \lesssim \tau_{exp} \ll \tau_w = \frac{0.5w^2}{D}$ to the fully developed solution for rectangular channels for $\tau_h \ll \tau_{exp} \lesssim \tau_w$. For long observation times, $\tau \geq \tau_w$, the side-wall-induced dispersion has sufficient time to fully spread across the channel. The dispersion for this case has been analytically worked out by many authors $[53–55]$, and is characterized by a Taylor diffusion constant of $k = \frac{7.951h^2u^2}{210D} = 0.038\frac{h^2u^2}{D}$ for channels with a large aspect ratio ($w/h \to \infty$).

For our experiments in Chapter 7, the observation time per molecule was typically $5–10$ s and we analyzed $\sim 100$ molecules for each datapoint, resulting in a total observation time of $\tau_{exp} = 500–1000$ s. For diffusion across the channel height we calculate $0.01 \leq \tau_h \leq 10$ s, where $\tau_h \approx 0.01$ s corresponds to the smallest channels and molecules in our experiments ($h = 107$ nm, $N = 8.8$ kbp) and $\tau_h \approx 10$ s for the biggest channels and molecules ($h = 3.8$ μm, $N = 48.5$ kbp). Similarly, we find for diffusion across $w$ timescales in the range $650 \leq \tau_w \leq 12 \cdot 10^3$ s, where $\tau_w \approx 650$ s corresponds to $h = 3.8$ μm and $N = 8.8$ kbp, and $\tau_w \approx 12 \cdot 10^3$ s to $h = 107$ nm and $N = 48.5$ kbp. With our experiments, we are somewhere in the middle of the intermediate timescale regime, depending on conditions. For simplicity, we used only the rectangular solution for point-like Taylor diffusion for comparison with our experiments of DNA dispersion in a slit-like channel (Chapter 7).

References


[16] We find \( Re = \frac{\mu u_{av} h}{\eta} = \frac{\Sigma p_{ext} h^3}{12 \eta} \approx 0.008 \) for an average fluid velocity of \( u_{av} = \frac{\Sigma p_{ext} h^2}{12 \eta} \approx 8 \text{ mm/s} \), calculated with numerical values \( h = 1 \mu m, \rho = 1000 \text{ kg/m}^3, \eta = 0.001 \text{ Pa-s} \) and \( \nabla p_{ext} = 10^8 \text{ Pa/m} \). These values correspond to typical experimental conditions.

[17] Eq. 2.24 also describes \( \psi_{PB}(z) \) for unequally charged surfaces of the same sign, if the boundary conditions are solved for both surfaces [12]. For this case, the origin of \( z \) is not in the center of the channel anymore.


[19] For a mixture of ions with different valences and for low surface potentials (\( \zeta < kT/Z e \) with \( Z \) the highest counterion valence), the solution to the Poisson Boltzmann equation (Eq. 2.10) results in an exponential decay of the potential with distance \( d \) from a single flat surface: \( \phi_{PB}(d) = \zeta e^{-\kappa d} \). The screening length \( 1/\kappa \) in this low-\( \zeta \) regime is defined by \( \kappa^2 = \frac{e^2}{\epsilon_0 kT} \sum_i n_i Z_i^2 \).


References


[40] The average length of the end-to-end vector, $\overline{R} = \langle R^2 \rangle^{1/2}$, characterizes the size of a polymer. Using Eq. 2.38 with $\langle r_n \cdot r_m \rangle = \langle r_n \rangle \cdot \langle r_m \rangle = 0$ for $n \neq m$, we find $\langle R^2 \rangle = \sum_{n,m=1}^{N} \langle r_n \cdot r_m \rangle = \sum_{n=1}^{N} \langle r_n^2 \rangle = Nb^2$, and $\overline{R} = b\sqrt{N}$. The average end-to-end vector is proportional to the radius of gyration, $R_g = b\sqrt{N/6} = \overline{R}/\sqrt{6}$, which is defined as the average segment distance from the center of mass [39].

[41] The delta function $\delta(r)$ has the property $\int_{-\infty}^{+\infty} f(r)\delta(r - a)dr = f(a)$. $\delta$ is not a continuous function, but it can be well approximated by the limit.
of the Cauchy distribution. For each orthogonal direction, we find \( \delta(x) = \lim_{a \to 0} \frac{a}{\pi a^2 + x^2} = \lim_{a \to 0} \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{ikx - |ak|} \, dk_x = \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{ikx} \, dk_x. \)

[42] The probability distribution in each orthogonal direction is \( \Phi_x(x, N) \simeq \left( \frac{3}{2\pi N b^2} \right)^{1/2} \exp \left( -\frac{3x^2}{2Nb^2} \right) \) for \( N \gg 1 \) and \( x \ll Nb \). Using \( \Phi = \Phi_x \Phi_y \Phi_z \) yields Eq. 2.44 for three dimensions.


We report measurements of the streaming current, an electrical current generated by a pressure-driven liquid flow, in individual rectangular silica nanochannels down to 70 nm in height. The streaming current is observed to be proportional to the pressure gradient and increases with the channel height. As a function of salt concentration, it is approximately constant below $\sim 10 \text{ mM}$, whereas it strongly decreases at higher salt. Changing the sign of the surface charge is found to reverse the streaming current. The data are best modeled using a nonlinear Poisson-Boltzmann theory that includes the salt-dependent hydration state of the silica surface.

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Chapter 3: Streaming Currents in a Single Nanofluidic Channel

3.1 Introduction

Nanofluidics is an emerging field of interest because of its potential to study and manipulate fluids, nanoparticles, and molecules in lab-on-a-chip devices [1–5]. Electrokinetic phenomena such as electro-osmotic flow and streaming currents [6–8], known to be induced by the charged walls of a microchannel, will become increasingly important in the nano regime because of the larger surface to volume ratio [9]. Moreover, new physical effects may occur as the counterion distributions of electrical double layers at opposite surfaces of a nanochannel start to overlap [10]. So far, the effects of surface charge and potential on electrokinetic fluid phenomena in confined nanostructures have been largely unexplored.

Streaming currents provide a useful technique for studying the electric properties of the solid-liquid interface as they result from the transport of counterions in the electric double layer by an applied pressure gradient [Fig. 3.1(d)]. It has also been suggested that streaming currents in fluidic channels may provide a simple and effective means of converting hydrostatic pressure differences into electrical energy [11], and that this process becomes particularly efficient in the nano regime where double layers overlap [10]. Streaming currents have been primarily studied on systems involving many channels in parallel, using materials such as sandstone cores [12], porous glass [11], and columns packed with latex beads [13]. While studies have appeared on single channels in the micron-range [6, 14, 15], nanofabrication now permits us to investigate streaming currents in well-defined, nanoscale geometries where double layers may overlap.

In this Letter, we report measurements of streaming currents in individual rectangular silica nanochannels as a function of pressure, channel height, and salt concentration. The data are compared with different models for the electrostatic properties of the surface: constant charge, constant potential, and a model that incorporates the chemical nature of the silica surface.

3.2 Device Fabrication & Methods

Nanofluidic channels were fabricated following a silicate bonding procedure similar to Stein et al. [9]. Channels 50 μm wide and 4.5 mm long were patterned between 1.5 × 1.5 mm² reservoirs on a fused silica substrate [Fig. 3.1(a)] by electron-beam lithography. The channels were plasma etched to a depth, h, ranging from 1147 nm down to 70 nm. After a thorough cleaning procedure that ended with a 1-minute dip in 0.5% aqueous HF solution, the channels were sealed by first spinning a 20 nm layer of sodium-silicate from 2% aqueous solution onto a flat fused silica chip and then pressing the silicate-coated surface to the patterned channel surface, and finally curing the device at 100°C for 2 hours. The
Figure 3.1: (a) Nanochannels are fabricated by bonding two pieces of fused silica. The top piece contains an etched nanochannel and two 1 mm diameter holes for fluid connections. (b) Side view of the nanochannel. (c) Streaming current as function of pressure for a 140 nm high channel at low and high salt concentrations. Lines are linear fits. (d) Schematic illustration of the origin of the streaming current.

channels were connected to a plexiglass holder using silicone O-rings to make a water-tight seal. Aqueous solutions, when inserted on one side of the holder, were drawn by capillary force into the nanochannels. Peek tubing connected one side of the channel to a pressurized chamber, while the opposite side was left open to atmosphere, as illustrated in Fig. 3.1(b). Electrical connections were established by inserting a Ag/AgCl electrode through a T-junction on the pressurized side, and a plain Ag/AgCl electrode wire into the liquid on the opposite side. The applied pressure was controlled to values of up to 4 bar using a Festo-LRP-1/4-4 pressure regulator and continuously monitored using a calibrated Honeywell 24PC pressure sensor. A correction was made for the small pressure drop of about 2% across the channel entrance and exit, which was simulated using fluid dynamics modeling software. Potassium chloride (KCl) solutions ranging from 5.6 \( \mu \text{M} \) to 1 M were made by the serial dilution of a 1 M KCl, 10 mM TRIS solution (pH = 8.0) with distilled de-ionized water (18 MΩ cm). A pressure of 4 bar was applied to remove any air bubbles from the channel and to achieve a stable streaming current. Approximately five hours of stabilization time were allowed after initially filling the channel, and about one hour for each subsequent exchange of salt solution. After stabilizing, streaming currents were measured while applying pressures that were varied from 1 to 4 bar in 80-second steps.
3.3 Measurements of the Streaming Current

The dependence of the measured streaming current, $I_{\text{str}}$, on the applied pressure across a 140 nm channel is plotted in Fig. 3.1(c) for salt concentrations of 17 $\mu$M and 0.33 M. Clearly $I_{\text{str}}$ scales linearly with pressure for both salt concentrations. We define a streaming conductance, $S_{\text{str}}$, as the streaming current per unit applied pressure. $S_{\text{str}}$ is clearly higher for the low KCl concentration, as can be seen from the slopes in Fig. 3.1(c). This contrasts the electrical conductance in nanochannels, which decreases at low salt [9].

Figure 3.2 shows $S_{\text{str}}$ as function of KCl concentration, $c$, for a 140 nm channel. Data points are averaged over two data sets and the error bars indicate the average standard deviation for all points. The data show that $S_{\text{str}}$ is approximately constant for $c$ below 10 mM, and decreases at higher $c$ where it has dropped by an order of magnitude at $c = 1$ M KCl. The same trend is observed for different channel heights as shown in Fig. 3.3, which shows $S_{\text{str}}$ versus $c$ for channels ranging from 70 to 1147 nm. The open symbols represent data points at very high molarity, where values for $S_{\text{str}}$ appear to be depressed. We attribute this to deviations from the mean-field model or to effects of surface roughness, as the double layer is very compact here. Higher channels are found to yield a larger streaming current. For all channel heights, $S_{\text{str}}$ reaches a constant value in the low-salt regime, and decreases at high salt. The low-salt plateau extends to higher $c$ for smaller channels.

3.4 Models of the Electrical Surface Properties

We begin modeling these data by equating the streaming current $I_{\text{str}}$ to the product of the charge density, $\rho(x)$, and the local speed of the fluid, $u(x)$, integrated over the cross section of the channel:

$$I_{\text{str}} = w \int_{-h/2}^{h/2} \rho(x)u(x)dx,$$

(3.1)

where $x$ is the height from the channel midplane, $w$ is the channel width and $h$ is the channel height. We ignore sidewall effects because $w \gg h$, and treat the flow and charge density profiles as uniform over the width of the channel, as in an infinite parallel-plate geometry. The velocity distribution is described by a Poiseuille flow subject to the no-slip boundary condition at the walls: $u(x) = -\frac{\Delta P}{8\eta L} (h^2 - 4x^2)$, where $L$ is the length of the channel, $\Delta P$ the pressure difference, and $\eta$ the viscosity. We describe $\rho(x)$ using nonlinear Poisson-Boltzmann
3.4 Models of the Electrical Surface Properties

Figure 3.2: Streaming conductance as a function of KCl concentration for a 140 nm high channel. Lines show model curves of constant surface charge, constant zeta potential, and the chemical equilibrium model, treated here in this Letter.

Figure 3.3: Streaming conductance as a function of KCl concentration for five different channel heights. Data points are averages of two data sets. The dashed lines represent the chemical equilibrium model for a single set of parameters, whereas the solid lines represent the same model when the parameters $C$ and $pK$ are different for each curve.
Chapter 3: Streaming Currents in a Single Nanofluidic Channel

theory, starting with the Poisson-Boltzmann equation for the electrostatic potential distribution $\psi(x)$:

$$\frac{d^2 \psi(x)}{dx^2} = \frac{kT \kappa^2}{e} \sinh \left( \frac{e\psi(x)}{kT} \right),$$

(3.2)

where $e$ is the electron charge, $k$ is the Boltzmann constant, $T$ is the temperature, and $\kappa^{-1}$ is the Debye screening length, defined by $\kappa^2 = \frac{2e^2n}{\epsilon \epsilon_0 kT}$. Here, $\epsilon_0$ is the permittivity of the vacuum, $\epsilon$ is the dielectric constant of water, and $n$ is the number density of the monovalent ions, proportional to $c$. The analytical solution for $\psi(x)$ is given by [16]:

$$\psi(x) = \psi_0 + \frac{2kT}{e} \ln \left( \text{JacCD} \left( \frac{z}{m} \right) \right),$$

(3.3)

where $\psi_0$ is the potential in the center of the channel, and $\text{JacCD}(z|m)$ is the Jacobi elliptical function with argument $z = \frac{e\psi_0}{kT}$ and parameter $m = e^{2e\psi_0/kT}$. The electric field, $E(x)$, and the charge density, $\rho(x)$, are obtained from $\psi(x)$ through $E(x) = -\frac{d\psi(x)}{dx}$ and Poisson’s equation, $\rho(x) = -\epsilon \epsilon_0 \frac{d^2 \psi(x)}{dx^2}$.

We now compare the predictions of this model for the streaming current, assuming different boundary conditions for the electrical surface properties: constant surface charge $\sigma$, constant zeta potential $\zeta$, or a chemically variable $\sigma$. Constant $\sigma$ is imposed using Gauss’ Law: $\sigma = \pm \epsilon \epsilon_0 E \left( x = \mp \frac{h}{2} \right)$, and constant $\zeta$ by specifying the potential at the no-slip plane: $\zeta = \psi \left( x = \pm \frac{h}{2} \right)$.

For any given $h$ and $\kappa$, Eq. (3.3) is solved using either of these boundary conditions to give a value for $\psi_0$, and thereby $\psi(x)$ and $\rho(x)$ are solved through Eq. (3.3) and Poisson’s equation. In the third model, we account for the chemical reactivity of the surface by allowing $\sigma$ to vary due to proton transfer through the following equilibrium [17]:

$$\text{SiOH} \rightleftharpoons \text{SiO}^- + \text{H}^+. \quad (3.4)$$

Behrens and Grier [16] developed a model for the diffuse layer potential, which we take to be $\zeta$, by describing the dissociation of SiOH groups using equilibrium constant, $pK$, and the compact Stern layer using capacitance, $C$, yielding the following relation for $\zeta$:

$$\zeta(\sigma) = \frac{kT}{e} \ln \left( \frac{-\sigma}{e \Gamma + \sigma} \right) + \ln \left( \frac{10}{e/kT} \right) (pK - pH) - \frac{\sigma}{C},$$

(3.5)

where $\Gamma$ is the surface density of chargeable sites. A second relation between $\zeta$
3.5 Model Comparison & Discussion

and \( \sigma \) derives from the charge and potential distribution in the diffuse layer. For
the case where \( h \gg \kappa^{-1} \), no double layer overlap occurs, and the surface charge
density is approximated using the Grahame equation:

\[
\sigma(\zeta) = \frac{2\epsilon\epsilon_0 kT \kappa}{e} \sinh \left( \frac{e\zeta}{2kT} \right)
\]  

(3.6)

Solving Eq. (3.5) and (3.6) yields a value for the surface charge \( \sigma \), or potential \( \zeta \). When double layer overlap does occur, no analytical solution is available. In
this case \( \psi(x) \), and thereby \( \zeta \), were solved for a set of \( \sigma \) values as a boundary
condition. \( \zeta \) was plotted as function of \( \sigma \), and its intersection point with the
chemical equilibrium relation, Eq. (3.5), was determined. The intersection point
yields self-consistent solutions for \( \sigma \) and \( \zeta \) that both depend on \( \kappa \) and \( h \). The \( \sigma \)
thus obtained was used as a boundary condition to find \( \rho(x) \) and \( S_{str} \). The model
predicts that \( \sigma \) increases with the salt concentration and that its dependence on
\( h \) is relatively unimportant for the channel sizes and salt concentrations that we
have used: at the lowest salt concentration, 5.6 \( \mu \)M, and the smallest channel,
70 nm, \( \sigma \) is predicted to be reduced by just 1.3% relative to the largest channel
of 1147 nm.

3.5 Model Comparison & Discussion

We now compare these three models for the streaming current in silica nanochannels. The predictions for \( S_{str} \) in a nanochannel as a function of \( c \) are plotted in
Fig. 3.2 for \( \zeta = -60 \) mV, \( \sigma = -4 \) mC/m², and the chemical equilibrium boundary
conditions with parameters \( \Gamma = 8 \) nm⁻², \( \text{pK} = 7.9 \), pH = 8 and \( C = 0.3 \) Fm⁻².
Note that the latter values are not free fit parameters, but were adopted from literature [18]. From Fig. 3.2, it is clear that the constant-\( \zeta \) line fails to describe our
data, as it is constant at high salt and drops when \( c \) is decreased below 100 \( \mu \)M. The constant-\( \sigma \) model, which previously described the salt dependence of the
electrical conductance successfully [9], does a somewhat better job: it yields a
plateau at low salt and drops off at high salt. However, the current decrease
sets in at significantly lower \( c \) (~1 mM) than observed (~10 mM), leading to
significant deviations between model and data. The chemical equilibrium model
gives the best fit over the full range of \( c \), predicting a roughly constant low-salt
plateau, and the correct high-salt decay.

In Fig. 3.3, the dashed lines represent predictions of the chemical equilibrium
model for the same single set of parameters that are applied to all curves [18].
This model describes the data reasonably well over 5 orders of magnitude in salt
Figure 3.4: Effect of the sign of the surface charge on the streaming current. The streaming current is shown as a function of pressure for a 279 nm-high nanochannel at low and high salt concentration. Data are shown for a negatively charged silica surface, and for a polylysine-coated surface which is positively charged. Lines indicate linear fits.

concentration and a factor of 16 in channel height, using a single set of material parameters. Since the properties of silica can vary between channels, we may fit the parameters pK and C for each curve [19] to obtain a very good description of $S_{str}$ for all channels, presented using solid lines.

We also demonstrate the sensitivity of the streaming current in nanochannels to the sign of the surface charge by inverting the surface charge. For this purpose, we coated a fused silica nanochannel with a layer of polylysine by incubating the channel in 0.01% 70-150 kDa polylysine solution for 12 hours, which is expected to render the surface positively charged. Indeed, Fig. 3.4 shows that $I_{str}$ in the direction of the liquid flow is negative for polylysine-coated channels, which indicates that the double layers are populated with negative ions, whereas the untreated silica surface generates a positive current, indicating positive ions in the double layer [20].

Finally, we comment on the proposal that the streaming-current effect can be used to convert hydrostatic energy into electrical energy [11]. Using the exact Poisson-Boltzmann solution for the charge distribution, combined with the chemical equilibrium boundary condition for the silica surface using a single set of material parameters [18], we find that a maximum energy conversion efficiency is obtained in the regime of double layer overlap. In aqueous solutions, this limits optimal channel dimensions to the submicron range. For example, for a
In conclusion, we have studied streaming currents in individual silica nanochannels with heights as small as 70 nm, and found that they increase linearly with applied pressure. The streaming current reverses direction when polylysine-coated, positively charged channel walls are used instead of negatively charged fused silica, emphasizing its sensitivity to the polarity of the surface charge. The streaming current increases with channel height, is approximately constant at salt concentrations below $\sim 10 \text{ mM KCl}$, and drops at higher salt. It can be modeled using nonlinear Poisson-Boltzmann theory, combined with a pressure-driven Poiseuille flow in a parallel-plate geometry. A chemical equilibrium model for the surface charge, taken as a boundary condition, predicts streaming currents in nanochannels fairly well over the full range of measured heights and KCl concentrations, whereas constant surface charge, and in particular constant potential boundary conditions, gave a poor description. This highlights the importance of using appropriate boundary conditions when dealing with electrokinetic phenomena in nanofluidics.

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References


[18] Reported values for the parameters in the chemical equilibrium model have ranges for \( \Gamma = 5 - 8 \) nm\(^{-2}\), \( pK = 6 - 8.5 \) and \( C = 0.2 - 2.9 \) Fm\(^{-2}\) [R.E.G. van Hal *et al.*, Adv. Coll. Int. Sci. **69**, 31 (1996), S. Ong *et al.*, Chem. Phys. Lett. **191**, 327 (1992) and Refs. [16, 17]]. \( \sigma \) is weakly sensitive to \( \Gamma \), and increases with \( C \) and pH – \( pK \). For pH – \( pK \) between −0.5 and +1.5 and \( C \) between 0.2 and 2.9 F/m\(^2\), we find extremes for \( \sigma \) at low salt between −2 and −8 mC/m\(^2\), and at high salt between −15 and −192 mC/m\(^2\). In all calculations we used values of \( \eta = 0.8904 \) mPas and \( \epsilon = 78.54 \) for water at 25°C, at which temperature our experiments were performed. Parameters \( \Gamma = 8 \) nm\(^{-2}\), \( pK = 7.9 \), pH = 8 and \( C = 0.3 \) Fm\(^{-2}\) predict the data best for all channel heights within the reported parameter space.
[19] Parameter values for the solid lines in Fig. 3: \( h = 70 \) nm → \( pK = 6.8 \), \( C = 0.26 \) Fm\(^{-2}\); \( h = 140 \) nm → \( pK = 7.8 \), \( C = 0.26 \) Fm\(^{-2}\); \( h = 279 \) nm → \( pK = 8 \), \( C = 0.2 \) Fm\(^{-2}\); \( h = 563 \) and \( 1147 \) nm → \( pK = 9 \), \( C = 0.9 \) Fm\(^{-2}\). \( \Gamma = 8 \) nm\(^{-2}\) and pH = 8 are kept constant.
[20] At low salt we observe that the streaming current of the polylysine-coated channel scales nonlinearly with the pressure. We speculate that long polymer chains at the wall may swell at low salt, thereby reducing the effective height, whereas at higher pressure, shear forces at the wall straighten out the polymers by fluid drag, thus increasing the effective height and streaming current.
Chapter 4

Charge Inversion at High Ionic Strength Studied by Streaming Currents

We report charge inversion, the sign reversal of the effective surface charge in the presence of multivalent counterions, for the biologically relevant regimes of divalent ions and mixtures of monovalent and multivalent ions. Using streaming currents, the pressure-driven transport of counter charges in the diffuse layer, we find that charge inversion occurs in rectangular silica nanochannels at high concentrations of divalent ions. Strong monovalent screening is found to cancel charge inversion, restoring the original surface charge polarity. An analytical model based on ion correlations successfully describes our observations.

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4.1 Introduction

Screening by counterions is of fundamental importance in mediating electrostatic interactions in liquids. For multivalent counterions ($Z$-ions, where $Z$ is the ion valency including the sign), a counterintuitive phenomenon is observed: Screening not only reduces the effective surface charge, but it can actually cause it to flip sign. This so-called charge inversion (CI) has been proposed to be biologically relevant in, e.g., DNA condensation, viral packaging, and drug delivery [1]. CI is not explained by conventional mean-field theories of screening. Recently, an analytical model was proposed that assumes that $Z$ ions form a two-dimensional strongly correlated liquid (SCL) at charged surfaces [2]. This effect is particularly strong for high $Z$, and was confirmed experimentally for $Z = 3$ and 4 [3]. Experimental evidence has remained inconclusive for the cases $Z = 2$ and mixtures of $Z$ ions with monovalent ions [4], both of which are biologically relevant given that K$^+$, Na$^+$ and Mg$^{2+}$ are the most abundant cations in the cell. The main difficulty is that existing experimental probes become unreliable at high concentrations ($\gtrsim 10$ mM): Electrophoretic mobility measurements suffer from increasingly low signal to noise at higher salt, whereas surface force measurements are complicated by short-range forces.

In this Letter, we investigate CI in individual silica nanochannels at high ionic strength by employing streaming currents as a new method. A streaming current is an ionic current that results from the pressure-driven transport of counterions in the diffuse part of the double layer [5], as illustrated in Fig. 4.1(b). The Stern layer, where the SCL is formed, is generally accepted to be immobile [6]. Consequently, streaming currents provide a direct measurement of the effective surface charge at the diffuse layer boundary. The well-defined rectangular channel geometry allows for straightforward interpretation. Contrary to other methods, streaming currents remain a reliable probe of the surface charge at high salt, up to 1 M in our experiments. We report unambiguous CI by divalent ions at concentrations above 400 mM. Additionally, we resolve the effect of screening by monovalent salt. We find that monovalent ions reduce CI by high-$Z$ ions, and even cancel CI entirely at sufficiently high monovalent ion concentrations. We successfully describe this behavior by an analytical model based on SCL theory.

4.2 Device Fabrication & Methods

Nanochannels, 50 $\mu$m wide and 4.5 mm long, were patterned between $1.5 \times 1.5$ mm$^2$ reservoirs using optical lithography, wet etched to a depth of 490 nm in fused silica, and sealed by a flat, fused-silica wafer with prefabricated holes.
using direct bonding (Micronit Microfluidics). Details of the experimental setup [Fig. 4.1(a)] and the streaming-current measurement procedure were described previously [5]. Streaming currents, generated by a known pressure gradient applied across the channel, were measured using Ag/AgCl electrodes. Trivalent cobalt(III)sepulchrate (CoSep; CoC\text{12}\text{H}\text{30}N\text{8}^{3+}), divalent calcium and magnesium (Ca\text{2+}; Mg\text{2+}), and monovalent potassium (K\text{+}) were used as the positive ionic species; chloride (Cl\text{−}) was the negative ion in each case. The desired ion concentrations were obtained by the serial dilution of concentrated solutions, prepared with 1 mM HEPES buffer (pH = 7.5) in distilled, deionized water (18 MΩcm).

### 4.3 Charge Inversion by Trivalent Ions

The measured streaming current was found to depend linearly on applied pressure. Examples for high (330 μM) and low (33 μM) CoSep concentrations [CoSep] are shown in Fig. 4.1(c). The streaming conductance, \( S_{str} \), defined as the streaming current generated per unit applied pressure in the direction of the pressure-driven fluid flow, was clearly positive for [CoSep]= 33 μM, indicating an excess of positive ions in the diffuse layer, and thus a negative effective surface charge. For [CoSep]= 330 μM, the sign of \( S_{str} \) was reversed, indicating a charge-inverted surface.
To establish streaming currents as a new technique for probing CI, we first turn our attention to the case of $Z = 3$, for which CI is well understood both experimentally and theoretically. The dependence of $S_{str}$ on [CoSep] reveals a rapid decrease of $S_{str}$ from positive to negative values at low concentrations [Fig. 4.2(a)]. The sign change indicates that CI has occurred, and from the crossover point (inset) we estimate the charge inversion concentration, $c_0$, to be $75 - 100$ $\mu$M. At higher [CoSep], $S_{str}$ decreased more slowly, reached a minimum near 10 mM, and increased slightly at higher concentrations. The surface remained charge-inverted up to the highest [CoSep] = 415 mM. While the three independent data sets consistently show the same qualitative trends, some hysteretic behavior and variations between the measurements were observed, which were attributed to slightly varying surface properties and ageing [7]. Similar effects were also seen in measurements with monovalent ions only.

Measurements of $S_{str}$ can be used to calculate the effective surface charge density $\sigma^*$, which can be readily compared to existing theoretical models and other experiments. We define $\sigma^* = \sigma_b + nZe$, where $\sigma_b$ is the bare silica charge density, and $n$ is the number density of $Z$ ions in the Stern layer. The no-slip plane is taken to be the boundary between the diffuse and Stern layers. $S_{str}$ is calculated to be $S_{str} = w \int_0^h \rho(x)u(x)dx$, where $h$ and $w$ are the channel height and width, $u(x)$ is the local fluid velocity per unit pressure, described by Poiseuille flow, and $\rho(x)$ is the local charge density in the diffuse layer, obtained from a numerical solution to the nonlinear Poisson-Boltzmann equation [5]. The resulting $\sigma^*$, plotted in Fig. 4.2(b), increased with [CoSep] from $\sim -16$ mC/m$^2$ at [CoSep] = 0 M to a maximum of $\sim +27$ mC/m$^2$ at [CoSep] $\geq 100$ mM [8].

We now compare the results of the streaming-current method for $Z = 3$ with existing theory and measurements. SCL theory in the absence of screening [2] predicts that $c_0$ should behave as:

$$c_0 = \left| \frac{\sigma_b}{2r_{ion}Ze} \right| \exp \left( \frac{\mu_c}{kT} \right),$$

where $r_{ion}$ is the ion radius, $kT$ is the thermal energy, $-e$ is the charge of an electron, and $\mu_c$ is the chemical potential that accounts for the ion correlations, given by $\mu_c = -kT \left( 1.65\Gamma - 2.61\Gamma^{1/4} + 0.26\ln \Gamma + 1.95 \right)$ [9]. The interaction parameter, $\Gamma = \sqrt{\frac{|\sigma_b|Z^3e^2}{4ekT\epsilon\epsilon_0}}$, where $\epsilon\epsilon_0$ is the electrical permittivity, is a measure of the energy relative to $kT$ that each ion gains upon the formation of a SCL. The condition $\Gamma \gg 1$ is required for the SCL-model to be valid [2]. Besteman et al. [3] demonstrated that the dependence of $c_0$ on surface charge, dielectrical constant,
Figure 4.2: (a) Three independent measurements of the streaming conductance $S_{str}$ as function of the CoSep concentration. The lines are guides to the eye. The open symbols indicate that $S_{str}$ regains positive values after each sweep from low to high concentration, although some hysteresis occurs. The inset highlights the charge inversion concentration region. (b) The effective surface charge $\sigma^*$ as function of the CoSep concentration, converted from $S_{str}$ as explained in the text.

and ion valence for $Z = 3$ and 4 can be described by Eq. (4.1). They found a $c_0$ of $170 - 300 \ \mu\text{M}$ for CoSep in aqueous solution on a silica bead, corresponding to $\sigma_b \approx -120 \ \text{mC/m}^2$ and $\Gamma = 5.7$ [10]. Our data yield a similar value of $c_0$: $75 - 100 \ \mu\text{M}$. This somewhat lower value can be explained by a slightly more negative $\sigma_b \approx -150 \ \text{mC/m}^2$, for which $\Gamma = 6.4$. Overall, our streaming-current results reproduce the findings for CI by trivalent ions well.
4.4 Charge Inversion by Divalent Ions

The reliability of streaming currents at high salt permits the study of CI by
divalent ions, for which results have been inconclusive so far [4]. In addition
to its clear relevance in biology, it is also interesting to investigate the role of
correlations in regimes where ions are more weakly interacting (Z = 2). Figure 4.3(a) shows our experimental demonstration of CI by two different divalent ion species, Ca$^{2+}$ and Mg$^{2+}$, which exhibit similar behavior. Between 3.3 μM and 1 M, $S_{str}$ decreased monotonically with salt concentration. We observed a sign reversal near 400 mM (inset), which is a clear indication of CI by divalent ions. $c_0$ was approximately 350 mM for Mg$^{2+}$ and 400 mM for Ca$^{2+}$ (inset). The small difference in the magnitude of $S_{str}$ between the two curves is within the typical range of reproducibility, and is not attributed to differences between the ion species, as it also appeared in the absence of either ion (at 0 M). The conversion of the $S_{str}$ data to $\sigma^*$ [Fig. 4.3(b)] shows a nearly constant $\sigma^*$ for both Mg$^{2+}$ and Ca$^{2+}$ below 30 mM, and a sharp increase at higher concentrations leading to CI above 400 mM. The scatter at low [Ca$^{2+}$] originates from saturation of the diffuse layer [8].

To compare our data with SCL theory for $Z = 2$, we naively apply Eq. (4.1) using $\sigma_b = -150$ mC/m$^2$ [11] to yield $\Gamma = 3.5$ and $c_0 = 47$ mM [10]. This prediction for $c_0$ is an order of magnitude lower than what was measured, which cannot be reconciled by slightly adjusting $\sigma_b$. The discrepancy between model and data confirms that the analytical SCL model is no longer valid for $Z = 2$. Further improvements to theoretical models will be needed to accurately describe CI for $Z = 2$. 

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Figure 4.3: Divalent ion concentration dependence of (a) the streaming conductance $S_{str}$ and (b) the effective surface charge $\sigma^*$. Lines are guides to the eye; open symbols indicate measurements after each sweep from low to high concentration. The inset highlights the charge inversion concentration region.
### 4.5 The Effect of Monovalent Salt on Charge Inversion

High concentrations of monovalent ions (∼ 150 mM) are typically present at physiological conditions in biological systems. It is unclear how this affects CI [4]. Using the streaming current as a reliable probe of CI, we can now access this regime experimentally. The dependence of $S_{str}$ and $\sigma^*$ on [KCl] in the presence of various CoSep ($Z = 3$) concentrations is shown in Fig. 4.4. Starting from a negative, charge-inverted value, $S_{str}$ was found to increase as function of [KCl], cross zero, reach a maximum between 50 – 300 mM KCl, and decrease at higher [KCl]. The observed dependence on [CoSep] is lost at 1 M KCl, where all curves converge. $\sigma^*$ was constant for low [KCl] up to 1 – 10 mM [Fig. 4.4(b)], and decreased sharply at higher concentrations where the screening length is dominated by the KCl (arrows). Upon approaching 1 M KCl, the decreasing trend in $\sigma^*$ was reversed.

For the physiological monovalent salt concentration of 150 mM, we found that CI did not occur, even for the highest investigated CoSep concentration of 1 mM. We can compare our results with an existing SCL model that includes screening [12]. This model treats $Z$ ions as point particles in a strongly correlated lattice at a distance $d$ from the surface, with lattice vectors $r_j$. Electrostatic screening is parametrized by the Debye screening length, $\kappa^{-1}$, defined by $\kappa^2 = \frac{e^2}{\epsilon \epsilon_0 kT} \sum_i c_i Z_i^2$, where $c_i$ and $Z_i$ are the bulk concentration and valency of ionic species $i$, respectively. The electrostatic free energy, $F$, is expressed as

$$F = \frac{\sigma_b^2}{2\epsilon \epsilon_0 \kappa} + \frac{\sigma_b n Z e}{\epsilon \epsilon_0 \kappa} e^{-\kappa d} + \frac{n Z^2 e^2}{8\pi \epsilon \epsilon_0} \alpha_{ZZ}, \quad (4.2)$$

where the parameter $\alpha_{ZZ} = \sum_{r_j \neq 0} e^{-r_j / r_j} + \sum_{r_j} \frac{e^{-\sqrt{r_j^2 + 4d^2}}}{\sqrt{r_j^2 + 4d^2}}$ accounts for the repulsive interactions between $Z$ ions and their image charges [12]. Minimizing $F$ by solving $\frac{\partial F}{\partial d} = 0$ and $\frac{\partial F}{\partial n} = 0$ yields the solutions $d_F$ and $n_F$, and thereby $\sigma^*$. Assuming a constant $\sigma_b = -150 \, \text{mC/m}^2$, we obtain $\sigma^* = +41$ and $+1041 \, \text{mC/m}^2$ for 10 and 1000 mM KCl, respectively. This prediction of strongly enhanced CI is in direct contradiction with the CI suppression that we observe (Fig. 4.4).

We can quantitatively improve the predictions of SCL theory in the presence of screening by including the entropy of mixing, $\mu_{id} = kT \ln \left( \frac{n}{2e^2 \epsilon_{ion}} \right)$, which was dropped from the original model for simplicity. This term accounts for the observed dependence of $\sigma^*$ on the bulk $Z$ ion concentration, $c$. Furthermore, we include $\Delta \mu^0$, the chemical potential difference between bulk and surface due to hydration and specific binding effects, and impose the extra condition $d \geq r_{ion}$. 


4.5 The Effect of Monovalent Salt on Charge Inversion

Figure 4.4: Effect of screening on charge inversion by trivalent ions. The streaming conductance $S_{str}$ (a) and the effective surface charge $\sigma^*$ (b) are plotted as function of KCl concentration for various CoSep concentrations. Solid lines are guides to the eye, while dashed lines are model curves for parameters $\sigma_b = -150$ mC/m$^2$, $r_{ion} = 445$ pm and $\Delta \mu^0 = +0.8kT$. Open symbols indicate measurements after the completion of each data set. Arrows show where the KCl contribution to the screening length equals that of the buffer and CoSep ions.

In equilibrium, the chemical potential difference between surface and bulk Z ions, $\Delta \mu$, becomes

$$\Delta \mu = \left. \frac{\partial F}{\partial n} \right|_{d = d_F^{cr}} + kT \ln \left( \frac{n}{2er_{ion}} \right) + \Delta \mu^0 = 0,$$

(4.3)

where $d_F^{cr}$ is the maximum of $d_F$ and $r_{ion}$ [13]. Finally, $n$ and $\sigma^*$ are solved using Eqs. (4.2) and (4.3). This improved model [dashed lines in Fig. 4.4(b)] successfully captures the [KCl] dependence of $\sigma^*$ up to [KCl] $\approx 30$ mM, including the concentration at which CI disappears. Note that we employ only one free
fit parameter, $\Delta \mu^0$, which turns out to be $\lesssim kT$, and assume a constant $\sigma_b$ \cite{11}. For $[\text{KCl}] \gtrsim 30$ mM, the model predicts a rapid decrease of $\sigma^*$ until $\sigma^* \approx \sigma_b$ [outside the range of Fig. 4.4(b)], whereas the measured $\sigma^*$ decreases much slower to a minimum and never reaches $\sigma_b$. At high monovalent salt concentrations, competition between monovalent and multivalent ions in the Stern layer \cite{14} and the complexation of a $Z$ ion with one of its counterions, effectively reducing the valence to $Z - 1$ \cite{15}, have been suggested to play roles. At 1 M KCl, monovalent screening in the Stern layer clearly dominates, as $\sigma^*$ is independent of the $Z$ ion concentration there (Fig. 4.4). These effects - which occur only at high salt - have not yet been described analytically, and our results provide an experimental base for future theoretical work. For intermediate salt concentrations, the SCL-model, including screening and the entropy of mixing, describes the monovalent ion dependency of CI quite satisfactorily.

4.6 Conclusion

In conclusion, we have demonstrated the method of streaming currents to be an excellent probe of charge inversion. We have exploited this technique to experimentally access the regime of high salt concentrations. We find that charge inversion occurs for high concentrations of divalent ions. Monovalent screening suppresses charge inversion, and even cancels it at high salt concentrations, including physiological conditions. An analytical model, based on the strongly correlated liquid picture, describes this effect well for low and intermediate salt levels if the entropy of mixing is included. At higher concentrations, screening of the bare surface charge becomes dominated by monovalent ions in the Stern layer.

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References


For $Z = 2$, some studies found the onset of CI (H.G. Bungenberg de Jong et al., Kolloid-Beihefte 42, 384 (1935); P. Kékicheff et al., J. Chem. Phys. 99, 6098 (1993); M. Quesada-Pérez et al., Mol. Phys. 100, 3029 (2002); T. Terao et al., Phys. Rev. E 63, 041401 (2001)), whereas others did not observe it (Q. Wen et al., J. Chem. Phys. 121, 12666 (2004); P.J. Scales et al., Langmuir 6, 582 (1990)). As function of monovalent salt concentration, both a reduction [14] and an increase [12] have been proposed.


[8] The conversion factor $\frac{\sigma^*}{\delta S_{str}}$ becomes very large, strongly amplifying small variations in $S_{str}$, when the counterions induced by $\delta \sigma^*$ are located very close to the surface, where they move slowly and barely contribute to $S_{str}$. This generally occurs at high salt, and sometimes at low salt when the diffuse double layer saturates at high zeta potentials due to the non-linear Poisson-Boltzmann solution. The conversion affects $c_0$ only slightly through small interpolation errors.


[10] In all calculations, a viscosity of 0.8904 mPas, and $\epsilon = 78.54$ for water at 25°C were used. Ionic radii are $r_{CoSep}=445$ pm (A. Bacchi et al, Acta Cryst. C49, 1163 (1993)) and $r_{divalent}=100$ pm, the average between $r_{Ca}=114$ pm and $r_{Mg}=86$ pm (R.D. Shannon et al, Acta Cryst. B25, 925 (1969)).

[11] We assume that $[H^+]$ at the surface, which determines $\sigma_b$ through a chemical equilibrium [5], is similar to the buffered bulk pH for low zeta potentials $\zeta$. Low $\zeta$ occurs around $c_0$ and for all datapoints in Fig. 4 ($|\zeta| < 18$ mV). In these cases, $\sigma_b$ should be roughly constant. We used $\sigma_b = -150$ mC/m² from the measured $c_0$ for $Z = 3$.


[13] For $\sigma_b = -150$ mC/m² and $Z = 3$, we obtain $d_F \approx 300$ pm. Imposing $d \geq r_{ion}$ yields $d_F = r_{CoSep}$ [10].


Chapter 5

Electrokinetic Energy Conversion Efficiency in Nanofluidic Channels

We theoretically evaluate the prospect of using electrokinetic phenomena to convert hydrostatic energy to electrical power. An expression is derived for the energy conversion efficiency of a two-terminal fluidic device in terms of its linear electrokinetic response properties. For a slit-like nanochannel of constant surface charge density, we predict that the maximum energy conversion efficiency occurs at low salt concentrations. An analytic expression for the regime of strong double layer overlap reveals that the efficiency depends only on the ratio of the channel height to the Gouy-Chapman length, and the product of the viscosity and the counterion mobility. We estimate that an electrokinetic energy conversion device could achieve a maximum efficiency of 12% for simple monovalent ions in aqueous solution.

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5.1 Introduction

A pressure-driven fluid flow through a narrow channel carries a net electrical charge with it, inducing both a current and a potential when the charge accumulates at the channel ends. These so-called streaming currents and streaming potentials can drive an external load, and therefore represent a means of converting hydrostatic energy into electrical power. The notion of employing such electrokinetic effects in an energy conversion device is not new [1], yet has received renewed attention in the context of micro- and nanofluidic devices [2–5], whose geometries and material properties can be engineered. High energy conversion efficiency and high output power are the requirements for such a device to be practical. Physical modeling of electrokinetic energy conversion is needed to guide the optimization of these properties.

Electrokinetic phenomena originate from a combination of two microscopic causes, illustrated in Fig. 5.1a, i) viscous forces couple the motion of dissolved ions to that of the surrounding fluid, and ii) charged channel surfaces induce the accumulation of counter ions into a screening layer of net opposite charge, called the double layer. It is conventional to model the distribution of electrostatic charge near a charged boundary using the Poisson-Boltzmann description of an electrolyte, and to couple its transport to that of the fluid using the Navier-Stokes equation. This theoretical framework has been used by several authors to calculate the theoretical energy conversion efficiency of fluidic devices, yielding maximum efficiencies ranging from \(\sim 0.1\%\) to \(\sim 1\%\) [1–4]. These calculations applied approximations that are only valid for the case of low electrostatic potentials and non-overlapping double layers, and assign a constant potential, called the \(\zeta\) potential, to parameterize the electrostatic condition of the surface. Recent investigations of ionic transport and streaming currents in well-defined, nanoscale fluidic channels have demonstrated how electrokinetic phenomena can be understood in the regimes of high surface potentials and overlapping double layers [5–8]. In these regimes, the full, non-linear Poisson-Boltzmann description of the electrolyte is needed. It was also confirmed that a constant \(\zeta\) potential boundary condition is a poor description of the silica surface under different salt and pH conditions, and that a constant or chemically reactive surface charge density is more appropriate [6, 7].

In this paper we present a theoretical analysis of electrokinetic energy conversion efficiency. We first provide an expression for the efficiency in terms of the measurable linear electrokinetic responses of any two-terminal fluidic device. We then calculate the efficiency for a particular geometry, namely a rectangular, slit-like channel, using the full Poisson-Boltzmann description of the electrolyte.
which includes the effects of double-layer overlap, and a constant surface charge density as an appropriate description of the surface. In contrast to previous work that used a constant $\zeta$ potential as a boundary condition, our model predicts the highest efficiency for low salt concentrations in nanoscale fluidic channels, where electric double layers overlap. An analytical expression for the efficiency in this important regime is presented. It reveals that the optimal efficiency results at a surface charge density that balances the tradeoffs between the increased charge transport and the increased electrical power dissipation that occur at high surface charge densities. We predict that channels can be optimized to deliver 12% energy conversion efficiency using aqueous solutions with common ions.
5.2 The Efficiency of a Fluidic Device of Arbitrary Geometry and Surface Charge

The electrokinetic properties of a fluidic device can be experimentally characterized by the response of the ionic current, $I$, and the fluid volume flow rate, $Q$, to either an applied pressure difference, $\Delta p$, or an applied electrochemical potential difference, $\Delta V$, across the device. We are interested in calculating the energy conversion efficiency in the linear response regime, where $I$ and $Q$ can be described by:

$$I = \frac{dI}{d\Delta p} \Delta p + \frac{dI}{d\Delta V} \Delta V \equiv S_{str} \Delta p + \frac{\Delta V}{R_{ch}} \quad (5.1)$$

$$Q = \frac{dQ}{d\Delta p} \Delta p + \frac{dQ}{d\Delta V} \Delta V \equiv \frac{\Delta p}{Z_{ch}} + S_{str} \Delta V \quad (5.2)$$

which define the constants: $R_{ch}$, the electrical resistance of the channel, $Z_{ch}$, the fluidic impedance of the channel, and $S_{str}$, the streaming conductance [6]. Linear electrokinetic behavior is expected as long as the electrostatic double layers are not significantly distorted by the fluid flows or by the applied electrostatic potentials [9]. Note that we have made use of the Onsager relation $\frac{dQ}{d\Delta V} = \frac{dI}{d\Delta p} \equiv S_{str}$, which is an expression of the reciprocity between electrically-induced fluid flows, and flow-induced electrical currents [9–11].

The ability of such a fluidic device to translate hydrostatic energy into electrical power, driven through a load resistance, $R_L$, can be calculated by analyzing the equivalent circuit presented in Fig. 5.1b. Under an applied pressure difference, $\Delta p$, the output streaming potential reaches an equilibrium value, $\Delta V = -\frac{R_{ch} R_L}{R_{ch} + R_L} S_{str} \Delta p$, from which the output power, $\Delta V^2/R_L$, is determined. The ratio of the output power to the input pumping power, $Q \Delta p$, is the electrokinetic energy conversion efficiency, $\mathcal{E}$. It is convenient to define a dimensionless parameter, $\alpha$, that provides a relative measure for the coupling between electrical and fluid transport:

$$\alpha \equiv S_{str}^2 Z_{ch} R_{ch}, \quad (5.3)$$

and a rescaled load resistance, $\Theta$, relative to the channel resistance:

$$\Theta \equiv \frac{R_L}{R_{ch}}. \quad (5.4)$$

In terms of these device characteristics, the electrokinetic energy conversion efficiency is given by:

$$\mathcal{E} = \frac{\alpha \Theta}{(1 + \Theta)(1 + \Theta - \alpha \Theta)}. \quad (5.5)$$
The maximum efficiency, \( \mathcal{E}_{\text{max}} \), achieved at a load resistance of \( \Theta = 1/\sqrt{1 - \alpha} \), is found to be

\[
\mathcal{E}_{\text{max}} = \frac{\alpha}{\alpha + 2 (\sqrt{1 - \alpha} + 1 - \alpha)}.
\]

(5.6)

\( \mathcal{E}_{\text{max}} \) increases from 0% at \( \alpha = 0 \) towards the limit of 100% as \( \alpha \) approaches 1, while conservation of energy requires that \( \alpha \leq 1 \). Interestingly, optimal energy conversion efficiency is achieved for \( R_L > R_{ch} \). By matching channel and load impedance, i.e. \( R_L = R_{ch} \), the system is instead optimized to deliver the maximum power for a given \( \Delta p \).

Because of the reciprocity between Eq. 5.1 and Eq. 5.2, this theory works equally well for describing the efficiency by which electrical energy is converted into fluid pumping power, an effect that is known as electro-osmotic pumping (fig. 5.1a) [12, 13]. By considering the pumping power of the electrokinetic device through a fluidic load impedance, \( Z_L \), a similar analysis determines the pumping efficiency to be the ratio of the output pumping power, \( \Delta p^2/Z_L \), to the input electrical power, \( I \Delta V \). By redefining \( \Theta \equiv Z_L/Z_{ch} \), Eqs. 5.5 and 5.6 are made to describe the efficiency of electro-osmotic pumping.

### 5.3 Calculations for a Slit-Like Nanochannel

The electrokinetic behavior of a fluidic device derives from its physical geometry, surface properties, and from the properties of the fluid filling it. In this section we calculate the electrokinetic energy conversion efficiency of a long, rectangular, slit-like fluidic nanochannel, whose channel walls are uniformly charged, and whose length \( L \), width \( w \), and height \( h \), satisfy \( L \gg h \) and \( w \gg h \) so that we can ignore end effects and treat the system as infinite parallel plates (fig. 5.1c and 5.1d). The channel is filled with aqueous solution of viscosity \( \eta \) and monovalent salt concentration \( n \). This particular system is chosen for several reasons: i) numerical calculations of electro-osmotic pumping indicated that the parallel-plate geometry has the highest efficiency [13], ii) the potential and charge distributions - described by Poisson-Boltmann theory - and the fluid velocity - described by a Poiseuille flow with no-slip boundary conditions - have exact solutions, and iii) rectangular channels with high aspect ratios [6, 7] and tunable microslits [14] have been used extensively to study electrokinetic effects.

The electrostatic potential, \( kT/\epsilon \psi(x) \), at height \( x \) from the channel midplane is described by the mean-field Poisson-Boltzmann equation for a monovalent salt,

\[
\frac{d^2 \psi}{dx^2} = \kappa^2 \sinh (\psi(x))
\]

(5.7)
where $\psi(x)$ is the dimensionless potential, $e$ is the electron charge, $kT$ is the thermal energy, $1/\kappa$ is the Debye screening length, defined by $\kappa^2 = 2e^2n/(\epsilon\epsilon_0 kT)$, and $\epsilon\epsilon_0$ is the permittivity of water. The analytical solution for $\psi(x)$ for a symmetrical channel can be expressed as [15, 16]:

$$
\psi(x) = \psi(0) + 2 \ln \left( \text{JacCD} \left( \frac{\kappa x}{2e} e^{-\psi(0)/2} \bigg| e^{2\psi(0)} \right) \right) \quad (5.8)
$$

where JacCD$(z|m)$ is the Jacobian elliptical function with argument $z$ and parameter $m$. This exact solution of $\psi(x)$ includes the effects of double-layer overlap and defines the density of positive and negative ions, $n_+$ and $n_-$, through the Boltzmann equation: $n_\pm(x) = ne^{\mp\psi(x)}$. The net charge density, $\rho(x)$, is found using Poisson’s equation, $\rho(x) = -\epsilon\epsilon_0 kT e \frac{\partial^2 \psi(x)}{\partial x^2}$.

The fluid flow induced by and contributing to the transport of ions is described by the Navier-Stokes equation

$$
\frac{d^2 u(x)}{dx^2} - \frac{\Delta V \epsilon_0 kT}{e} \frac{d^2 \psi(x)}{dx^2} + \frac{\Delta p}{L} = 0, \quad (5.9)
$$

where $u(x)$ is the fluid velocity at height $x$. A no-slip boundary condition is imposed at the channel walls, $x = \pm h/2$. Solving Eq. 5.9 for $\Delta V = 0$ or $\Delta p = 0$ yield, respectively, the pressure-driven velocity profile $u_p(x) = \frac{\Delta p}{8\eta L}(h^2 - 4x^2)$, and the electro-osmotic velocity profile $u_V(x) = \frac{\Delta V \epsilon_0 kT}{\eta} \psi(x) - \zeta$, where $\zeta$ is the potential at the no-slip plane.

Eq. 5.7-5.9 form the basis for calculating $Z_{ch}$, $R_{ch}$, and $S_{str}$, which define the energy conversion efficiency through eqs. 5.3-5.5, using the following expressions for a slit-like channel:

$$
\frac{1}{Z_{ch}} = \frac{w}{\Delta p} \int_{-h/2}^{h/2} u_p(x) dx = \frac{wh^3}{12\eta L} \quad (5.10)
$$

$$
\frac{1}{R_{ch}} = \frac{w}{\Delta V} \int_{-h/2}^{h/2} \left( \frac{\Delta V}{L} \sum_i e n_i(x) \mu_i + \rho(x) u_V(x) \right) dx \quad (5.11)
$$

$$
S_{str} = \frac{w}{\Delta p} \int_{-h/2}^{h/2} \rho(x) u_p(x) dx, \quad (5.12)
$$

where $\mu_i$ and $n_i$ are the electrophoretic mobility and the density of ion species $i$, respectively. The fluidic impedance (Eq. 5.10) is the familiar result for Poiseuille flow in a slit-like channel, and should apply as long as the Navier-Stokes equation (Eq. 5.9) is valid [17]. The behavior of $R_{ch}$ and $S_{str}$ is nontrivial, and has recently been investigated in silica nanochannels [6, 7]: The electrical conductance (Eq. 5.11) consists of contributions from electrophoretic ion transport through the
5.3 Calculations for a Slit-Like Nanochannel

Figure 5.2: KCl concentration dependence of $E_{\text{max}}$ for channel heights $h = 75$ (grey curves) and 490 nm (black curves), and surface charge densities $\sigma = -10$ (solid curves) and $-2$ mC/m$^2$ (dashed curves), calculated using the exact expressions of eqs. 5.3-5.13 with the parameters specified in [18]. These results account for both co- and counterions, and include the effects of double-layer overlap.

fluid, and convective transport of charge. $R_{\text{ch}}$ was found to exhibit a surface-charge-governed low-$n$ plateau due to the transport of counter ions in the double layer, and a decrease with increasing $n$ in the high-$n$, bulk transport regime. These results for silica were best described by applying a constant surface charge density, $\sigma$, as a boundary condition [7]. The streaming conductance (Eq. 5.12) exhibits a low-$n$ plateau in the double-layer-overlap regime, which is also captured by a constant-$\sigma$ boundary condition, and a decay at high $n$, which was best modeled by a chemical equilibrium model of $\sigma$ [6].

These experiments on silica nanochannels indicate that a constant $\sigma$ is a good description of the electrostatic condition of the channel walls at low salt, a fair approximation at high salt, and in all cases better than assuming a constant $\zeta$. We therefore impose a constant surface charge density of the channel walls, which relates to $\psi(x)$ through Gauss’ Law:

$$\sigma = \pm \frac{\epsilon_0 k T}{e} \left. \frac{d\psi(x)}{dx} \right|_{x = \pm h/2}. \quad (5.13)$$

Eqs. 5.3-5.13 are exact and valid for all channel heights, including the regime of double layer overlap. These equations were evaluated numerically using Maple to generate the plots in Fig. 5.2 and 5.3: First, the potential distribution (Eq. 5.8)
is calculated for a given channel height, salt concentration, and the boundary condition of a constant $\sigma$ (Eq. 5.13). This potential is then used to calculate the electrokinetic response properties through eqs. 5.10-5.12, from which $\alpha$ (Eq. 5.3) and $E_{\text{max}}$ (Eq. 5.6) are finally obtained.

Fig. 5.2 shows the calculated salt dependence of $E_{\text{max}}$ for channels filled with an aqueous solution of potassium chloride (KCl). For $h = 75$ nm and $h = 490$ nm channels with fixed surface charge densities, the highest $E_{\text{max}}$ occurs in a low-$n$ plateau, followed by a decay to zero efficiency at high $n$. The plateau region extends to higher $n$ for smaller channels: up to $n = 10^{-5}$ M for a $h = 490$ nm channel, and up to $n = 10^{-4}$ M for a $h = 75$ nm channel. The height of the plateau clearly depends on both $h$ and $\sigma$, as can be seen by comparing the curves in Fig. 5.2.

The high energy conversion efficiency that occurs at low salt conditions can be understood intuitively: At sufficiently low $n$, where $\kappa h \ll 1$, electrostatic forces expel co-ions from the channel, leaving only counter ions. Because co-ions do not add to the generated electrical power by streaming currents, but instead provide an additional pathway for power dissipation through ionic conductance, they can only detract from the energy conversion efficiency. The power and streaming current are both maximal for low $n$, where the current originates from the transport of counterions that are induced by the fixed surface charge.

Fig. 5.3 shows $E_{\text{max}}$ as function of $h$ and $\sigma$, calculated using eqs. 5.3-5.13 for a low salt concentration of $10^{-5}$ M KCl, where the efficiency should be close to its low-$n$ plateau value of fig. 5.2. $E_{\text{max}}$ is found to have a maximum as function of both $h$ and $\sigma$ (Fig. 5.3). For fixed $\sigma$, $E_{\text{max}}$ increases quickly from zero at $h = 0$ nm to a peak of about 7% before decaying slowly with $h$, both for $\sigma = -2$ mC/m$^2$ and $\sigma = -10$ mC/m$^2$. The peak in $E_{\text{max}}$ shifts to higher $h$ as $\sigma$ decreases: It occurs at $h \approx 250$ nm for $\sigma = -2$ mC/m$^2$, and at $h \approx 60$ nm for $\sigma = -10$ mC/m$^2$. A similar behavior of $E_{\text{max}}$ is seen for fixed $h$ and changing $\sigma$ (inset): the peak efficiency shifts to higher $\sigma$ when $h$ decreases. The peak value of 7% barely depends on $h$ for small channels. Only for higher $h$ is the peak efficiency slightly reduced (to $\sim 6\%$ for $h = 490$ nm).

### 5.4 The Limit of Strong Double-Layer Overlap

The electrokinetic energy conversion efficiency peaks as a function of channel height and surface charge density in the low salt regime because of the competition between two opposing effects: As $\sigma$ is raised, the increased counter ion density results in an increased convective charge transport by a pressure-driven
5.4 The Limit of Strong Double-Layer Overlap

Figure 5.3: Channel height and surface charge density dependence of $E_{\text{max}}$, calculated for $10^{-5}$ M KCl using the exact expressions of eqs. 5.3-5.13, which include the effects of double layer overlap. The main panel shows $E_{\text{max}}$ as function of $h$ for high ($\sigma = -10 \text{ mC/m}^2$) and low ($-2 \text{ mC/m}^2$) surface charge densities. The inset plots $E_{\text{max}}$ as function of $\sigma$ for the channel heights 75, 200 and 490 nm. As $n$ is only $10^{-5}$ M, the calculated $E_{\text{max}}$ in this figure is close to the low-$n$ plateau values in fig. 5.2.

Flow (enhancing power generation), while also providing a path for resistive power dissipation. The scaling of these effects with $\sigma$ depends on the distribution of counter ions across the fluid velocity profile, which determines the optimal surface charge density for a given channel height. This interplay, as well as the influence of ion mobility and fluid viscosity, is clearly revealed by an analytic approximation that we derive for the low salt limit: In the absence of co-ions, which occurs when $\kappa h \ll 1$, the analytic solution to the Poisson-Boltzmann equation (Eq. 5.7) simplifies to [16]:

$$\psi (x) = 2 \ln \left[ \cos \left( \frac{Kx}{2} \right) \right] + \psi (0), \quad (5.14)$$

where the inverse length $K \equiv \kappa e^{-\psi (0)/2}$ [19] contains an integration constant, $\psi (0)$. The electrostatic potential distribution is fully specified by imposing the constant-surface-charge boundary condition (Eq. 5.13), which gives

$$\frac{Kh}{4} \tan \frac{Kh}{4} = \frac{h}{2\lambda}. \quad (5.15)$$
The Gouy-Chapman length, $\lambda = 2\epsilon_0 kT/|\sigma|$, defines a layer within which most counterions are localized. By inserting Eq. 5.14 into the expressions for $Z_{ch}$, $R_{ch}$ and $S_{str}$ (eqs. 5.10-5.12), we obtain an analytical expression for $\alpha$, as defined in Eq. 5.3:

$$\alpha = \frac{3}{K_h^4 \tan \frac{K_h}{4}} \left( \frac{4}{K_h} \int_0^{K_h/4} y \tan(y) dy \right)^2 - \frac{\mu \eta e}{2\epsilon_0 kT},$$

(5.16)

from which the maximum efficiency (Eq. 5.6) can be calculated directly. The efficiency in the regime of strong double layer overlap, when solved for the case of a constant surface charge density (Eq. 5.15), only depends on the following two dimensionless parameters: i) $\mu \eta e/2\epsilon_0 kT$, which contains the fluid and ion properties $\eta$ and $\mu$, and ii) $h/2\lambda$, which explains the reciprocal behavior of $h$ and $|\sigma|$ observed in Fig. 5.3.

The competing effects of ionic and streaming conductance result in a peak value of $E_{max}$ at $h/2\lambda \approx 8$, or equivalently at $h|\sigma| \approx 0.6 \text{ nm} \times \text{C/m}^2$, as can be seen from the solid lines in Fig. 5.4. Calculations of $E_{max}$ using eqs. 5.3-5.13 with Cl\(^-\) as the co-ion, $n = 10^{-5}$ M, and a fixed $\sigma = -10 \text{ mC/m}^2$ yield curves that are indistinguishable from these solid lines, demonstrating the validity and accuracy of Eq. 5.16 for low but realistic salt concentrations. Since the highest $E_{max}$ occurs for a relatively high surface charge, i.e. $h/2\lambda \gg 1$, we can estimate $K$ in the high-$\sigma$ limit, $h/2\lambda \to \infty$, which implies $Kh/4 \to \pi/2$ from Eq. 5.15. Expanding Eq. 5.15 in a Laurent series around $Kh = 2\pi$ gives:

$$K \approx \frac{2\pi}{2\lambda + h} + O \left( \frac{Kh}{4} - \frac{\pi}{2} \right).$$

(5.17)

This high-$\sigma$ approximation for $\psi(x)$ in the absence of co-ions leads, through Eqs. 5.11 and 5.12, to the following approximations of the ionic resistance and the streaming conductance:

$$\frac{1}{R_{ch}} \approx \frac{w}{L\eta} \left( \frac{2\epsilon_0 kT}{e} \right)^2 \left( 1 + \frac{\mu \eta e}{2\epsilon_0 kT} \right) \frac{2}{\lambda},$$

(5.18)

$$S_{str} \approx \frac{w}{L\eta} \frac{2\epsilon_0 kT}{e} h \left[ \frac{2\lambda}{h} + 1 \right] \ln \left( 1 + \frac{h}{2\lambda} \right) - 1,$$

(5.19)

The ionic conductance, which dissipates power, is proportional to the surface charge density (Eq. 5.18) since $|\sigma| \propto 1/\lambda$, whereas $S_{str}$, which is responsible for electrical power generation, increases linearly for small $|\sigma|$, and logarithmically as function of large $|\sigma|$ (Eq. 5.19). $R_{ch}$ and $S_{str}$ are used to approximate the electrokinetic energy conversion efficiency through Eq. 5.3 and 5.6, yielding
Figure 5.4: Calculated $\mathcal{E}_{\text{max}}$ dependence on the degree of Gouy-Chapman-layer overlap in the low salt limit (no co-ions) for three counter ion types. The solid lines represent the exact solution of Eq. 5.16, and the dashed lines represent the approximation of Eq. 5.20. Calculations using eqs. 5.3-5.13 with $\text{Cl}^-$ as the co-ion, a low salt concentration of $n = 10^{-5}$ M, and a fixed $\sigma = -10$ mC/m$^2$ yield curves that are indistinguishable from the solid lines. The bottom axis shows the $h/2\lambda$-dependence, and the top axis the equivalent $h|\sigma|$-dependence. Inset: The peak value of $\mathcal{E}_{\text{max}}$ as function of the counter ion mobility relative to the case of potassium ions ($\mu = \mu_{\text{K}^+}$) in water ($\eta = \eta_w$). The circles indicate ions of different mobility in aqueous solution. The values of the physical parameters used in the calculations appear in [18]. The same curve for $\mathcal{E}_{\text{max}}$ is obtained when plotted against the renormalized viscosity, $\eta/\eta_w$, with constant $\mu = \mu_{\text{K}^+}$ [20].

$$\mathcal{E}_{\text{max}} \approx \frac{3}{4} \frac{2\lambda}{\mu} \left[ \frac{2\lambda}{\mu} + 1 \right] \ln \left( 1 + \frac{h}{2\lambda} \right) - 1 \right]^2 + O \left( \frac{2\lambda}{h} \right)^2. \quad (5.20)$$

This simple expression for the efficiency captures the most important features of the exact solution, as seen in the comparison presented in fig. 5.4: (i) $\mathcal{E}_{\text{max}}$ increases linearly for small $h/2\lambda$, peaks at $h/2\lambda \approx 8$, and finally decreases at higher $h/2\lambda$, and (ii) the efficiency is higher for counterions with a lower mobility.

The shape of $\mathcal{E}_{\text{max}}$ as function of $h/2\lambda$ is explained by the gradual shift from a homogeneous counter ion distribution for small surface charge densities to a strong counter ion accumulation close to the surface for high surface charge den-
sities. In the low-salt regime (no co-ions), the number of counterions in the nanochannel is proportional to the surface charge density due to the imposed charge neutrality, which explains the linear relation, $1/R_{ch} \propto |\sigma|$, from Eq. 5.18. When these counterions are distributed homogeneously across the channel, they probe the fluid velocity profile evenly, which yields the same proportional scaling for the streaming conductance, $S_{str} \propto |\sigma|$. The linear increase of $E_{max}$ with surface charge in the low-$\sigma$ limit then follows from $E_{max} \propto R_{ch}S_{str}^{2}$ [21]. For high surface charge densities, the counterions become localized very close to the charged channel walls where they barely contribute to the streaming conductance due to the low fluid speed there. In this limit of very high $\sigma$, $E_{max}$ becomes dominated by the channel resistance which decreases as $1/|\sigma|$.

The efficiency increases with decreasing ion mobility (Fig. 5.4) because ionic conductance leads to power dissipation. Peak efficiency values of 2%, 7%, and 12% are obtained for aqueous solutions containing H$^+$, K$^+$, and Li$^+$, respectively. This maximal efficiency, found by solving $\frac{\partial E_{max}}{\partial (h/2\lambda)} = 0$, depends only on the remaining parameter, $\frac{\mu_{eq}}{\frac{\sigma_{eq}}{T}}$ [22], and is plotted as function of the rescaled ion mobility for aqueous solution in the inset of figure 5.4. Because the mobility of Li$^+$ is the lowest among simple monovalent ions, 12% represents the upper limit of the electrokinetic energy conversion efficiency predicted for an aqueous system with common ions. This efficiency can be further improved to around 20% using more complex monovalent ions such as tetra-$n$-amylammonium$^+$ (TAmA$^+$).

The preceding calculations of electrokinetic power generation and efficiency neglect the possible effects of “Stern conductance” [23]. This electrical conductance is invoked to explain the differences that are often seen between the electrical surface properties inferred from different types of electrokinetic measurements, and is assumed to occur in the Stern layer, the first molecular layers directly adjacent to a hard surface where liquid and ion properties may differ from the bulk values and where mean-field Poisson-Boltzmann theory breaks down. The conventional microscopic picture of Stern conductance is that ions in the Stern layer are mobile in response to an electric field, but not to a pressure gradient [23]. As Stern conductance can only act to reduce the efficiency as it provides an additional pathway for power dissipation, the predicted efficiencies in this paper may be regarded as upper limits. Indeed, recent experiments on the energy conversion efficiency in rectangular silica nanochannels, which we will present elsewhere [24], reveal a reduction in efficiency due to the presence of a Stern conductance, although they confirm other predictions by this paper such as the peak in efficiency at low salt. It is not known whether Stern conductance is a general feature of all materials, but it is clearly an important material parameter to consider when designing nanochannels for an optimal efficiency.
5.5 The Electrical Output Power of a Macroscopic Device

We now calculate the electrical power that could in principle be obtained from a compact (hand-held) electrokinetic energy conversion device. The hypothetical device consists of a 1 mm-thick, 10 cm × 10 cm glass filter that consists of an array of parallel rectangular, slit-like nanochannels. The output power is proportional to the area of this filter, as it scales linearly with the number of parallel channels and the channel width. The height of each nanochannel is 500 nm, small enough for strong double layer overlap at low salt (\( \kappa h \ll 1 \)), and the channel surface charge is optimized for maximum energy conversion efficiency (\( h/2\lambda \approx 8 \)). The filter porosity - the fraction of the filter area available for fluid flow - is taken to be 50%. For an applied pressure \( \Delta p = 5 \) bar, the output power of this device is calculated to be 2.6 W for Li\(^+\) as the counter ion in aqueous solution.

5.6 Conclusions

Based on general considerations, we have shown how a fluidic system’s efficiency at converting hydrostatic potential energy to electrical power depends on its linear electrokinetic response properties. Calculations of the electrokinetic properties of slit-like nanochannels based on the Poisson-Boltzmann description of the electrostatics and the Navier-Stokes description of the fluid reveal that the efficiency is maximal at low salt concentrations. In the regime where double layers overlap, co-ions are expelled, and their power-dissipating effects are avoided. In this low-salt limit, the energy conversion efficiency only depends on the product of the fluid viscosity and the counter ion mobility, and on the ratio of the channel height to the Gouy-Chapman length. A peak in the efficiency at \( h/2\lambda \approx 8 \) results from opposing effects of the counterion distribution on streaming conductance and ionic conduction, and its magnitude is enhanced with decreasing ion mobility and fluid viscosity. For an aqueous-based system containing Li\(^+\) ions, a maximum energy conversion efficiency of 12% is predicted, as is Watt-level electrical power from a compact device requiring an applied pressure difference of 5 bar.

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5.7 Appendix A - The Onsager Relation

In this appendix we present the results from the electrokinetic response model for the hypothetical case when the Onsager relation, \( Q_{eol} \equiv dQ/d\Delta V = dI/d\Delta p \equiv S_{str} \), would not be valid, and discuss the potential implications on the interpretation of electrokinetic energy conversion measurements, in particular those presented in Chapter 6.

The Onsager relation was formally proven in the linear electrokinetic response regime for arbitrary topology, symmetry and heterogeneity, by applying the Navier-Stokes equations for an incompressible fluid with the no-slip boundary condition to model the fluid flow, Poisson’s equation to model the charge distribution, and the Boltzmann distribution for a constant chemical potential in thermodynamical equilibrium to model the ionic concentrations [9]. Our expressions for the linear response properties for the slit-like geometry, eqs. 5.10-5.12, derive from the same equations, and the Onsager relation was therefore correctly applied in this chapter. Indeed, explicit calculations of the electro-osmotic flow rate through \( Q_{eol} = w \int_{-h/2}^{h/2} u_V(x) dx \) yield exactly the same numerical values as Eq. 5.12.

Real systems may not in all cases be governed by the above mentioned mean-field equations. In particular, in the Stern layer of a few molecular layers adjacent to a charged surface, the molecular nature of water and ions must be taken into account: It is generally assumed that the fluid in the Stern layer is stagnant, while the ions move upon applying electrical fields. Clearly, several assumptions which underlie the proof of the Onsager relation break down in this case: the mobile ions do not couple their motion to the surrounding fluid, and the charge distribution is not described by Poisson-Boltzmann theory. However, in our measurements presented in Chapter 6, the Stern conductance was still found to respond linearly upon applied potential and pressure gradients, allowing the application of the linear electrokinetic response model. In Chapter 6, we analyzed the efficiency of our experiments by assuming the Onsager relation to hold true. In this appendix, we will discuss what happens to the calculated efficiency if the Onsager relation would break down.

We introduce the Onsager parameter, \( \gamma = \frac{Q_{eol}}{S_{str}} \), and redefine \( \alpha \) in this appendix as \( \alpha = S_{str} Q_{eol} Z_{ch} R_{ch} \) for symmetry reasons between the cases of power generation and electro-osmotic pumping. Of course, this new definition of \( \alpha \) will only lead to different results if \( \gamma \neq 1 \), and does not affect the plots and discussions in sections 5.1 – 5.6. The definition for the dimensionless load resistor, \( \Theta = \frac{R_{L}}{R_{ch}} \) (Eq. 5.4), is not changed. The efficiency for power generation, \( \eta_{power} \), for a system
with linear electrokinetic responses is then given by

\[
\varepsilon_{\text{power}} = \frac{\Delta V^2 / R_L}{Q \Delta p} = \frac{\Theta R_{ch}}{(1+\Theta)^2} \frac{S_{str}^2 \Delta p^2}{\Theta Z_{ch} - \frac{\Theta R_{ch}}{1+\Theta} Q_{\text{coef}} S_{str} \Delta p^2} \\
= \frac{1}{Q_{\text{coef}} S_{str} R_{ch} Z_{ch}} \frac{1}{1+\Theta} \frac{\alpha \Theta}{(1+\Theta)(1+\Theta - \alpha \Theta)} = \frac{\varepsilon}{\gamma} \tag{5.21}
\]

For pumping across a fluidic load admittance, \(Z_L\), we find the equilibrium pressure \(\Delta p = -\frac{Z_{ch} Z_L}{Z_{ch} + Z_L} Q_{\text{coef}} \Delta V\), and define the dimensionless load admittance as \(\Theta = \frac{Z_L}{Z_{ch}}\). The pumping efficiency is then expressed as

\[
\varepsilon_{\text{pump}} = \frac{\Delta p^2 / Z_L}{I \Delta V} = \frac{\Theta Z_{ch}}{(1+\Theta)^2} \frac{Q_{\text{coef}}^2 \Delta V^2}{\Theta Z_{ch} - \frac{\Theta Z_{ch}}{1+\Theta} Q_{\text{coef}} S_{str} \Delta V^2} \\
= \frac{1}{Q_{\text{coef}} S_{str} R_{ch} Z_{ch}} \frac{1}{1+\Theta} \frac{\alpha \Theta}{(1+\Theta)(1+\Theta - \alpha \Theta)} = \gamma \varepsilon \tag{5.22}
\]

Clearly, the efficiency for power generation and pumping are different if \(\gamma \neq 1\): \(\varepsilon_{\text{power}}\) is reduced while \(\varepsilon_{\text{pump}}\) is enhanced for \(\gamma > 1\).

We now investigate the the effect of \(\gamma \neq 1\) on measurements of the efficiency. So far, the highest experimentally obtained energy conversion efficiency was reported as \(\varepsilon_{\text{max}} \approx 3\%\) [Chapter 6]. For the regime of \(\varepsilon_{\text{max}} \lesssim 3\%\), the maximum efficiency of Eq. 5.6 is well approximated by its linearization around 0, \(\varepsilon_{\text{max}} \simeq \alpha/4\).

![Figure 5.5: \(\varepsilon_{\text{max}}\) as function of \(\alpha\). The solid line represents Eq. 5.6. The dashed line is \(\varepsilon_{\text{max}} = \alpha/4\).](image)
(see Fig. 5.5). Including the Onsager parameter into the linear approximation of the maximum efficiency, yields for power generation

\[
E_{\text{max, power}} \approx \frac{\alpha}{4\gamma} = \frac{S_{\text{str}}^2 R_{ch} Z_{ch}}{4},
\]

(5.23)

and for electro-osmotic pumping

\[
E_{\text{max, pump}} \approx \frac{\gamma\alpha}{4} = \frac{Q_{\text{eof}}^2 R_{ch} Z_{ch}}{4}.
\]

(5.24)

These equations show that the effect of \( \gamma \neq 1 \) is already implicitly accounted for in the linear regime of \( E_{\text{max}} \), if \( \alpha \) is defined as \( S_{\text{str}}^2 R_{ch} Z_{ch} \) for power measurements (Eq. 5.3), and as \( Q_{\text{eof}}^2 R_{ch} Z_{ch} \) for pumping measurements. Our experiments on the efficiency of power generation indeed used Eq. 5.3 to analyze \( E_{\text{max}} \), as \( Q_{\text{eof}} \) could not be measured directly. Similarly, in pumping experiments usually only the pumping flow rate, \( Q_{\text{eof}} \), is measured, in which case also for pumping \( \gamma \neq 1 \) is implicitly corrected for.

### 5.8 Appendix B - Ions of Arbitrary Valence

In this appendix we derive the analytical expression for \( \alpha \) in the regime of strong overlap for arbitrary ion valence \( Z \) (including the sign). This corresponds to Eqs. 5.14-5.16 in the paper, where only the results for \( Z = 1 \) were shown. Here, we include more intermediate steps to guide the reader.

Before we start our derivation, some remarks on the potentially complicating effects of multivalent ions (\( Z \)-ions) are appropriate. First of all, \( Z \)-ions are known to accumulate strongly in the Stern layer, thereby affecting and potentially reversing the effective surface charge. This effect of charge inversion occurs only at high bulk concentrations for divalent ions (Chapter 4), but already much sooner for \( Z \geq 3 \) [25, 26]. It should therefore be kept in mind that \( \sigma \) is typically not a material parameter that is unaffected by the ions in solution, but rather a property that may depend quite strongly on the ion concentration, particularly for high-\( Z \) counterions. Secondly, an analytical expression for the Poisson-Boltzmann equation exists only for a symmetrical \( Z : Z \)-salt. This is typically not the case: some monovalent ions will always be present in aqueous solutions (protons, hydroxide ions), and most salts containing \( Z \)-ions are asymmetric, i.e., the valence of the anions and cations is not the same, leading to a different charge distribution in the double layer at positive and negative surfaces. Fortunately, for strong double-layer overlap the picture becomes greatly simpli-
A nonzero electrostatic potential is present across the whole channel volume, enhancing the counterion density while reducing the co-ion density through the Boltzmann equation. When this potential is sufficiently large - for strong overlap and a large enough $\sigma$ - the co-ions can be neglected. The Boltzmann equation also predicts that the concentration of high-$Z$ counterions is more strongly enhanced than that of ions with a lower valency. Therefore, the counterion species with the highest-$Z$ will be dominant in a nanochannel with large $\sigma$ and strong double-layer overlap.

We solve the Poisson-Boltzmann equation between parallel plates for a solution containing only counterions of valence $Z$ and bulk concentration $n$. All other ions, present in the bulk, are assumed to be of negligible concentration in the regime of strong-double layer overlap. To simplify all equations we define the dimensionless potential $\psi(x) = \frac{Z e}{kT} \Psi(x)$. Note that $\psi(x)$ is negative, because $Z$ and $\Psi(x)$ are of opposite sign. The charge density, $\rho(x)$, is defined by Poisson’s equation,

$$\rho(x) = -\epsilon_0 \frac{\partial^2 \Psi(x)}{\partial x^2} = -\epsilon_0 kT \frac{\partial^2 \psi(x)}{\partial x^2},$$

and also by Boltzmann’s equation,

$$\rho(x) = \sum_i Z_i e n_i e^{-\frac{Z_i e \psi(x)}{RT}} = Z e n e^{-\psi(x)}.$$

Combining Eq. 5.25 and 5.26 yields the Poisson-Boltzmann equation for a single ion species of valence $Z$:

$$\frac{\partial^2 \psi(x)}{\partial x^2} = -\frac{Z^2 e^2 n}{\epsilon \epsilon_0 kT} e^{-\psi(x)}.$$

For a symmetrical salt, for which $\kappa = \sqrt{\frac{2Z^2 e^2 n}{\epsilon \epsilon_0 kT}}$, this equation reduces to

$$\frac{\partial^2 \psi(x)}{\partial x^2} = -\kappa^2 e^{-\psi(x)},$$

which corresponds to the familiar Eq. 5.7 when co-ions are ignored. Multiplying both sides of Eq. 5.27 with $\frac{\partial \psi(x)}{\partial x}$ and inserting $\frac{\partial^2 \psi(x)}{\partial x^2} \frac{\partial \psi(x)}{\partial x} = \frac{1}{2} \frac{\partial}{\partial x} \left[ \left( \frac{\partial \psi(x)}{\partial x} \right)^2 \right]$ and $e^{-\psi(x)} \frac{\partial \psi(x)}{\partial x} = -\frac{\partial}{\partial x} \left[ e^{-\psi(x)} \right]$ yields

$$\frac{\partial}{\partial x} \left[ \left( \frac{\partial \psi(x)}{\partial x} \right)^2 \right] = \frac{2Z^2 e^2 n}{\epsilon \epsilon_0 kT} \frac{\partial}{\partial x} \left[ e^{-\psi(x)} \right].$$
Integrating both sides gives
\[
\left( \frac{\partial \psi(x)}{\partial x} \right)^2 = \frac{2Z^2e^2n}{\varepsilon_0 kT} e^{-\psi(x)} - K^2.
\] (5.29)

For symmetry reasons, \( \frac{\partial \psi(x)}{\partial x} = 0 \) at \( x = 0 \) for identical surfaces, which yields the integration constant \( K^2 = \frac{2Z^2e^2n}{\varepsilon_0 kT} e^{-\psi(0)} \). This definition of \( K \) for arbitrary \( Z \) corresponds to the \( K \) defined in the main text (for \( Z = 1 \)). Rewriting Eq. 5.29 in the differential form yields
\[
\frac{K}{2} \partial x = e^{-\frac{\psi(x)}{2}} \frac{d\psi(x)}{\sqrt{e^{-\psi(x)} - e^{-\psi(0)}}} = \partial \left[ \arcsin \left( e^{\frac{\psi(x) - \psi(0)}{2}} \right) \right]. \] (5.30)

Integrating yields
\[
\frac{Kx}{2} = \arcsin \left( e^{\frac{\psi(x) - \psi(0)}{2}} \right) + C, \] (5.31)

where the integration constant \( C = -\frac{\pi}{2} \) is found by solving \( \psi(x) = \psi(0) \) for \( x = 0 \). Rewriting yields the dimensionless potential distribution for strong double layer overlap,
\[
\psi(x) = 2 \ln \left[ \cos \left( \frac{Kx}{2} \right) \right] + \psi(0). \] (5.32)

We impose the constant-\( \sigma \) boundary condition at the channel walls using Gauss’ Law, \( \sigma = \pm \varepsilon_0 \frac{\partial \psi(x)}{\partial x} \bigg|_{x=\pm h/2} = \pm \varepsilon_0 kT \frac{\partial \psi(x)}{\partial x} \bigg|_{x=\pm h/2} \), which leads, through \( \frac{\partial \psi(x)}{\partial x} = -K \tan \left( \frac{Kx}{2} \right) \), to the boundary condition for the dimensionless potential,
\[
\frac{Kh}{4} \tan \frac{Kh}{4} = h \frac{1}{2\lambda}, \] (5.33)

where \( \lambda = -\frac{2\varepsilon_0 kT}{Zn} \) is the Gouy-Chapman length for ions of arbitrary valency. Note that \( Z \) and \( \sigma \) are always of opposite sign, and that \( \lambda \) is therefore always positive. Eq. 5.32 and Eq. 5.33 are exactly the same as Eq. 5.14 and Eq. 5.15, respectively, and reveal that the shape of the dimensionless potential across the nanochannel - set by \( \frac{Kh}{4} \) - only depends on the degree of Gouy-Chapman overlap, \( \frac{h}{2\lambda} \). The dimensionless potential is thus affected by \( Z \) only through its effect on \( \lambda \). Note that the valency also affects the ratio between the real and dimensionless potentials.

We now continue our derivation to obtain \( \alpha \), taking the solution of the dimensionless potential, Eqs. 5.32-5.33, as a starting point to calculate the electrokinetic properties. Inserting the second derivative of the potential, \( \frac{\partial^2 \psi(x)}{\partial x^2} = \frac{-K^2}{2\cos^2 \left( \frac{Kx}{2} \right)} \),
into Eq. 5.25 yields the charge density,

\[ \rho(x) = \frac{\epsilon \epsilon_0 kT K^2}{2Ze} \frac{1}{\cos^2 \left( \frac{Kx}{2} \right)}. \]  

(5.34)

The linear electrokinetic properties are calculated using Eqs. 5.10-5.12, and expressed as function of \( Kh/4 \) to allow easy incorporation into a formula for \( \alpha \) at the end of this paragraph. Inserting Eq. 5.34 into the expression for the streaming conductance, Eq. 5.12, yields

\[
S_{\text{str}} = \frac{w}{\Delta p} \int_{-h/2}^{h/2} \rho(x)u_P(x)dx \\
= \frac{w \epsilon \epsilon_0 kT K^2}{8\eta L} \frac{K^2}{Ze} \frac{1}{2} \int_{-h/2}^{h/2} h^2 - 4x^2 \cos^2 \left( \frac{Kx}{2} \right) dx \]

(5.35)

\[
= \frac{hw \epsilon \epsilon_0 kT}{\eta L} \frac{4}{4} \int_0^{Kh/4} y \tan(y)dy,
\]

where we employed \( \int_{-h/2}^{h/2} h^2 - 4x^2 \cos^2 \left( \frac{Kx}{2} \right) dx = \frac{128}{K^2} \int_0^{Kh/4} y \tan(y)dy \) to simplify the final expression. The channel conductance, Eq. 5.11, for a single ion species of local density \( n(x) \) and mobility \( \mu \) is expressed as

\[
\frac{1}{R_{ch}} = \frac{w}{\Delta V} \int_{-h/2}^{h/2} \left( \frac{\Delta V}{L} \mu Zen(x) + \rho(x)u_V(x) \right) dx.
\]

(5.36)

The first part of the integral, representing the conductance through the electrophoretic mobility of the ions, becomes

\[
\frac{\mu w}{L} \int_{-h/2}^{h/2} Ze n(x)dx = \frac{\mu w}{L} \int_{-h/2}^{h/2} \left( \frac{\Delta V}{L} \frac{\epsilon \epsilon_0 kT}{Ze} \psi(x) - \psi(\pm h/2) \right) dx = \frac{\mu w 8\epsilon \epsilon_0 kT Kh}{\eta L} \frac{4}{4} \tan \left( \frac{Kh}{4} \right),
\]

(5.37)

where \( \sigma \) was written as function of \( \frac{Kh}{4} \) using Eq. 5.33. The second part, which represents the convective transport of charge due to the electro-osmotic flow, is found using \( u_V(x) = \frac{\Delta V}{L} \frac{\epsilon \epsilon_0 kT}{Ze} \frac{1}{ \eta L} \left[ \psi(x) - \psi(\pm h/2) \right] \) for the electro-osmotic flow velocity for arbitrary \( Z \), and Eq. 5.34 for \( \rho(x) \):

\[
\frac{w}{\Delta V} \int_{-h/2}^{h/2} \rho(x)u_V(x)dx = \frac{w}{\eta L} \left( \frac{\epsilon \epsilon_0 kT}{Ze} \right)^2 \frac{K^2}{2} \int_{-h/2}^{h/2} \psi(x) - \psi(\pm h/2) \cos^2 \left( \frac{Kx}{2} \right) dx \\
= \frac{w}{\eta Lh} \left( \frac{4\epsilon \epsilon_0 kT}{Ze} \right)^2 \left[ \frac{Kh}{4} \tan \left( \frac{Kh}{4} \right) - \left( \frac{Kh}{4} \right)^2 \right].
\]

(5.38)

Here, we used \( \int_{-h/2}^{h/2} \frac{\psi(x) - \psi(\pm h/2)}{\cos^2 \left( \frac{Kx}{2} \right)} dx = 2 \int_{-h/2}^{h/2} \frac{\ln \left[ \cos \left( \frac{Kx}{2} \right) \right]}{\cos^2 \left( \frac{Kx}{2} \right)} dx \).
### Table 5.1: Limiting molar ionic conductivities, $\lambda^0$, in aqueous solution at 25°C, taken from L. Coury, Curr. Sep. 18, 3 (1999). TBUA$^+$ means Tetra-$n$-butylammonium$^+$. $\lambda^0$-values are typically lower for smaller $Z$, except for H$^+$ and OH$^-$ whose mobility is exceptionally high due to their interactions with water molecules.

<table>
<thead>
<tr>
<th>Ion Type</th>
<th>$\lambda^0$</th>
<th>Ion Type</th>
<th>$\lambda^0$</th>
<th>Ion Type</th>
<th>$\lambda^0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TBUA$^+$</td>
<td>19.5</td>
<td>UO$_2^{2+}$</td>
<td>64</td>
<td>Al$^{3+}$</td>
<td>183</td>
</tr>
<tr>
<td>Li$^+$</td>
<td>38.7</td>
<td>Mg$^{2+}$</td>
<td>106</td>
<td>Fe$^{3+}$</td>
<td>204</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>50.1</td>
<td>Ca$^{2+}$</td>
<td>119</td>
<td>La$^{3+}$</td>
<td>209.1</td>
</tr>
<tr>
<td>K$^+$</td>
<td>73.5</td>
<td>CO$_3^{2-}$</td>
<td>138.6</td>
<td>Fe(CN)$_6^{3-}$</td>
<td>302.7</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>76.4</td>
<td>Pb$^{2+}$</td>
<td>142</td>
<td></td>
<td></td>
</tr>
<tr>
<td>OH$^-$</td>
<td>199.1</td>
<td>SO$_4^{2-}$</td>
<td>160</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H$^+$</td>
<td>349.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$2h\left(\tan\left(\frac{K\eta}{4}\right) - 1\right)$ to write the expression as function of $\frac{K\eta}{4}$. The channel conductance is the sum of Eq. 5.37 and 5.38:

$$\frac{1}{R_{ch}} = \frac{w}{\eta L h} \left(\frac{4\epsilon_0 k T}{Z e}\right)^2 \left[\frac{K\eta}{4}\tan\left(\frac{K\eta}{4}\right)\left(1 + \frac{Z e \mu Z}{2\epsilon_0 k T}\right) - \left(\frac{K\eta}{4}\right)^2\right]. \quad (5.39)$$

Inserting the expressions for the linear electrokinetic properties into the expression for $\alpha$, Eq. 5.3, while applying the Onsager relation $Q_{eoff} = S_{str}$ yields the analytical result for arbitrary $Z$:

$$\alpha = \frac{3}{K\eta} \int_0^{K\eta/4} y \tan(y) dy \right)^2 \right. \left. \frac{K\eta}{4}\tan\frac{K\eta}{4}\left(1 + \frac{Z e \mu Z}{2\epsilon_0 k T}\right) - \left(\frac{K\eta}{4}\right)^2. \quad (5.40)$$

This expression for alpha is equal to Eq. 5.16, except that the dimensionless parameter, $\frac{Z e \mu Z}{2\epsilon_0 k T}$, now depends on $Z$.

We now discuss the effect of the ion valence on the efficiency. Fig. 5.4 accurately represents the efficiency as function of $\frac{h}{2\lambda}$ also for multivalent ions, if $\mu Z$ instead of $\mu$ is used to characterize the counterions (replacing $\mu$ with $\mu Z$ in Eq. 5.16 yields exactly Eq. 5.40). We find that the optimal efficiency for a Z-ion is found at $\frac{h}{2\lambda} \approx 8$, or equivalently at $h\sigma = -0.6$ nm×C/m² (note that the top axis in Fig. 5.4 becomes $-h\sigma Z$ with the new definition of $\lambda$). For ions with higher $Z$, the optimal efficiency thus occurs in smaller channels or for smaller $\sigma$, assuming all other parameters constant. This optimal efficiency at $\frac{h}{2\lambda} \approx 8$ is higher for smaller $\frac{Ze\mu Z}{2\epsilon_0 k T} \propto \mu Z$. The limiting molar ionic conductivity, $\lambda^0 \propto \mu Z$, can be
used to directly compare different ions in terms of their energy conversion ability (the x-axis of the inset in Fig. 5.4 can then be read as $\lambda_0^\alpha/\lambda_0^{\alpha+}$). Table 5.1 shows that $\lambda_0$ is typically smaller for lower $Z$. Monovalent ions are therefore expected to yield the highest electrokinetic energy conversion efficiencies.

References

[18] We used viscosity $\eta_w = 0.93$ mPas and relative permittivity $\epsilon = 79$ for water, and temperature $T = 296.15$ K. The ion mobilities $\mu_{K^+} = 7.32$, $\mu_{Li^+} = 3.86$, $\mu_{H^+} = 34.8$, $\mu_{Na^+} = 4.99$ and $\mu_{Cl^-} = -7.60 \times 10^{-8}$ m$^2$/Vs were


[20] Unlike the efficiency, the output power exhibits a different scaling for \( \eta \) and \( \mu \), as the input power roughly scales with \( 1/\eta \) and is independent of \( \mu \). Reducing the viscosity therefore increases the output power much stronger compared to reducing \( \mu \).

[21] The relation \( E_{\text{max}} \propto R_{ch} S_{str}^2 \) is accurate for the range of efficiencies in Figure 5.4. The linear response of \( E_{\text{max}} \) (Eq. 5.16) in the limit \( h/2\lambda \to 0 \) is found to be \( E_{\text{max}} \approx \frac{1}{12} \frac{2e\sigma kT h}{\mu \nu e} \frac{h}{2\lambda} = \frac{h|\sigma|}{24\mu \eta} \).

[22] The terms in the sum in Eq. 5.18 represent the convective and conductive contributions to the electrically driven ion transport with a ratio of \( 1 : \frac{\mu \nu e}{2e\sigma kT} \). The dimensionless parameter \( \frac{\mu \nu e}{2e\sigma kT} \) thus represents the relative importance of the ionic conduction compared to the electro-osmotic ion transport [7]. Minimizing this parameter improves the efficiency (inset of Figure 5.4).


Chapter 6

Power Generation by Pressure-Driven Transport of Ions in Nanofluidic Channels

We report on the efficiency of electrical power generation by means of streaming currents, the pressure-driven transport of counterions in the electrical double layer. Our experimental study of individual rectangular silica nanochannels as function of salt concentration and channel height reveals that the highest efficiency occurs in the regime of double layer overlap, with up to $\sim 3\%$ efficiency for a 75 nm-high channel. The data are well described by Poisson-Boltzmann theory with an additional electrical conductance of the Stern layer.

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This chapter has been submitted to Physical Review Letters: F.H.J. van der Heyden, D.J. Bonthuis, D. Stein, C. Meyer and C. Dekker.
6.1 Introduction

A pressure-driven flow through a fluidic channel induces a flow of counter charges in the double layer at the channel walls, thus generating an electrical current (Fig. 6.1a). When this so-called streaming current is driven through an external load resistor $R_L$, electrical energy is harvested from the fluidic system. The notion of employing streaming currents to generate electrical power is not new [1], yet has received renewed attention in the context of micro- and nanofluidic devices [2–6] whose geometries and material properties can be engineered.

The power output and energy conversion efficiency, $\mathcal{E}$, have been modeled for fluidic devices with a known geometry by calculating their electrokinetic response properties using the Navier-Stokes description of the fluid flow, and Poisson-Boltzmann (PB) theory of the electrostatic ion distribution in the diffuse layer [1–5, 7]. Approximations of the PB solution with a constant surface potential $\zeta$ as the electrical boundary condition [1–4] have predicted an increase of $\mathcal{E}$ as function of salt concentration $n$ [3]. In contrast, we recently calculated that $\mathcal{E}$ decreases as function of $n$, based on an exact solution of PB with a constant surface charge $\sigma$ as a more appropriate boundary condition for silica [5]. This theory also predicts that i) $\mathcal{E}$ is independent of $n$ in the regime of strong double layer overlap, i.e., for low $n$ in nanoscale channels, ii) $\mathcal{E}$ decreases as function of the counterion mobility, and iii) $\mathcal{E}$ does not depend strongly on the channel height as long as double layers overlap [8]. Experimental studies of electrokinetic power generation have focused on porous glass because its many parallel channels make this material a good candidate for obtaining appreciable powers [4]. However the poor control over the geometry and surface properties in porous silica complicates quantitative testing of the physical models.

In this Letter, we present an experimental study of electrokinetic power generation in the well-defined geometry of individual rectangular nanofluidic channels down to the regime where double layers overlap. Our measurements of the generated streaming potential $\Delta V$ across the nanochannel as function of applied pressure $\Delta p$ and $R_L$ are excellently described by a linear electrokinetic response model. The highest power (up to 240 pW for a single 490 nm-high channel) and efficiency (up to 3.2% for a 75 nm-high channel) are found for low $n$. The energy conversion efficiency of our silica channels is limited by a Stern layer conductance of $10 – 30$ pS, which provides an additional pathway for power dissipation.
6.2 Device Fabrication & Methods

Nanochannels of width \( w = 50 \, \mu\text{m} \), length \( L = 4.5 \, \text{mm} \) and height \( h \) (Fig. 6.1b) were fabricated between \( 1.5 \times 1.5 \, \text{mm}^2 \) reservoirs in fused silica using a direct bonding method [9]. Details of the experimental set-up and the streaming current measurement procedure are described elsewhere [10]. Potassium chloride (KCl) and Lithium Chloride (LiCl) solutions were prepared by the serial dilution of a 1 M stock solution with 10 mM HEPES buffer (pH = 7.5) in distilled, de-ionized water (18 MΩcm). A load resistor \( R_L \), adjustable between 0.1 and 100 GΩ in steps of 0.1 GΩ, was connected between the Ag/AgCl electrodes at each channel end (Fig. 6.1c). The potential difference \( \Delta V \) across \( R_L \) was measured for each applied pressure difference \( \Delta p \).

6.3 The Effect of the Load Resistor

The voltage difference \( \Delta V \), generated when a pressure-driven streaming current flows through an external load resistor, is observed to increase linearly with \( \Delta p \) for various KCl concentrations, [KCl] (Fig. 6.2a). For a constant \( \Delta p \), \( \Delta V \) is found to increase with \( R_L \) (Fig. 6.2b) until reaching a saturation value at high \( R_L \). \( \Delta V \) was higher for lower [KCl] across the full range of load resistances. Fig. 6.2c reveals that the generated power \( P = \frac{\Delta V^2}{R_L} \), calculated from the data in Fig. 6.2b,
peaks at a particular value of $R_L$. The highest power from a single 490 nm-high silica nanochannel was $\sim 240$ pW, obtained for $R_L = 55 \, \text{G} \Omega$ and $[\text{KCl}] = 10^{-5}$ M. $\Delta V$ and $P$ did not change with $n$ for $[\text{KCl}] \lesssim 10^{-4.5}$ M [11].

We model the energy conversion ability of our fluidic channel by the electrical equivalent circuit of Fig. 6.2d [5]. The channel device is characterized through its electrokinetic response properties, which relate the liquid volume flow $Q$ and the electrical current $I$ to the applied driving forces $\Delta p$ and $\Delta V$. We define the streaming conductance $S_{str} \equiv \frac{dI}{d\Delta p}$ [10], the electrical resistance $R_{ch} \equiv \frac{d\Delta V}{dI}$, and the fluidic impedance $Z_{ch} \equiv \frac{d\Delta p}{dQ} = \frac{12\eta L}{w h^3}$ for a slit-like channel containing a fluid of viscosity $\eta$. The potential difference for a given $\Delta p$ is calculated to be $\Delta V = -\frac{R_{ch} R_L}{R_{ch} + R_L} S_{str} \Delta p$. We observe from Fig. 6.2a that $\Delta V$ scales linearly with $\Delta p$ for constant $R_L$. The expression for $\Delta V$ is fitted to the measurements as function of $R_L$ with constant $\Delta p$ (Fig. 6.2b), yielding $S_{str}$ and $R_{ch}$ as fit parameters at each salt concentration. The excellent quality of the fits confirms that the nanochannel is accurately characterized by its linear electrokinetic responses. Independent measurements of $R_{ch}$ - measured by a V-I sweep - and $S_{str}$ just before and after the power measurement corresponded to the fit values within a few percent. The equivalent circuit model predicts maxima in the power and efficiency as function of $R_L$, given by $P_{\text{max}} = \frac{R_{ch} S_{str}^2 \Delta p^2}{4}$ at $R_L = R_{ch}$, and $\mathcal{E}_{\text{max}} = \frac{2}{2 - \alpha + 2\sqrt{1 - \alpha}}$ at $R_L = \frac{R_{ch}}{\sqrt{1 - \alpha}}$ with $\alpha = \frac{S_{str}^2 Z_{ch} R_{ch}}{R_L}$, respectively [5].

The saturation behavior of $\Delta V$ as function of $R_L$, and the resulting maxima in $P$ and $\mathcal{E}$, can be understood intuitively by considering the model circuit of Fig. 6.2d: For small load resistors ($R_L \ll R_{ch}$), the streaming current, $S_{str} \Delta p$, will mainly flow through $R_L$, generating a small potential difference proportional to $R_L$, $\Delta V \approx -S_{str} \Delta p R_L$, whereas for very large load resistances ($R_L \gg R_{ch}$), most current will flow back through the channel itself, generating the saturation potential $\Delta V \approx -S_{str} \Delta p R_{ch}$. The increase of $P$ for small $R_L$, the decrease for high $R_L$, and the maximum in between then follow directly from $P = \frac{\Delta V^2}{R_L}$. Since the energy conversion efficiency is defined as the output power $P$ divided by the input power, which is mainly consumed by viscous dissipation, $\mathcal{E}$ and $P$ show nearly identical behavior as function of $R_L$ (Fig. 6.2c).
6.3 The Effect of the Load Resistor

![Diagram of a nanochannel with a load resistor and connections](image)

Figure 6.2: Measurements for various KCl concentrations in a 490 nm-high silica nanochannel of (a) $\Delta V$ as function of $\Delta p$ for $R_L = 50 \text{ G} \Omega$, and (b) $\Delta V$ and (c) $P = \Delta V^2 / R_L$ as function of $R_L$ for $\Delta p = 4 \text{ bar}$. Lines are fits to the equivalent electronic circuit model of the nanochannel connected to $R_L$, as depicted in (d). The fit parameters $S_{str}$ and $R_{ch}$ are used to calculate the efficiency (inset). We define $\Delta p = p_2 - p_1$ and $\Delta V = V_2 - V_1$. The arrows indicate the ionic current directions for a positive applied $\Delta p$ during power generation.
6.4 The Salt Concentration and Channel Height Dependence

Figure 6.3 shows our experimental study of $E$ as function of salt concentration, channel height and counterion type in individual rectangular nanofluidic channels. It reveals that the highest efficiency occurs in the regime of double layer overlap. $S_{str}$ and $R_{ch}$ (Figs. 6.3a and 6.3b) are obtained through fits of $\Delta V$ versus $R_L$ for each measured salt concentration, from which $P_{max}$ and $E_{max}$ are calculated (Figs. 6.3c and 6.3d). The streaming conductance was approximately constant with salt concentration at low $n$ and then dropped at higher $n$. The channel conductance on the other hand was constant at low $n$ and increased at higher $n$ [11]. $P_{max}$ and $E_{max}$ were about constant at low $n$, and decreased strongly at higher $n$. The transition between these salt regimes occurred at higher salt concentrations for smaller channels, viz., at $10^{-3.5}$ M for $h = 75$ nm versus $10^{-1.5}$ M for $h = 490$ nm. In the regime of maximum efficiency and power (low $n$), we found that $R_{ch}$ and $E_{max}$ were 2-3 times larger for the small channels, whereas $S_{str}$ and $P$ were respectively one and two orders of magnitude larger for the big channels (Table 6.1). Changing the counterion type in the same channel barely affected the conductance for low $n$ [12]. For high $n$, KCl resulted in a $\sim 30\%$ higher conductance than LiCl, which is consistent with the difference in bulk conductivity.

Figure 6.3 (right page): Experimental results for $S_{str}$, $1/R_{ch}$, $P_{max}$ and $E_{max}$ as function of salt concentration with $\Delta p = 4$ bar. Numbered colors indicate different measurements, with the channel height and ion type indicated in (c). 3 and 4 are our experiments with the highest power and efficiency, respectively. 1 and 2 are typical for changing the counterion type in the same channel. The right axes in (a) and (c) correspond to 4. Open symbols indicate that the bulk conductivity was affected by protons for $n = 10^{-5}$ [11]. Lines represent different electrical boundary conditions for the silica surface: a constant $\sigma = -8.2$ mC/m$^2$ (dashed lines; insets), a constant $\zeta = -100$ mV (dotted lines; insets) and a chemically-varying $\sigma$ with either $G_{Stern} = 0$ (dash-dotted lines; insets) or $G_{Stern} \neq 0$ (solid lines; main panels). The dash-dot-dotted curves in (b) indicate the bulk conductance. The parameter values for the chemically-varying $\sigma$ model [13] with fixed $\Gamma = 8$ nm$^{-2}$ and pH = 7.5 were found to be $pK = 8.2$; 8.3; 8.4; 7.5 and $C = 0.8$; 2.5; 2.9; 0.15 Fm$^{-2}$, and $G_{Stern}$ was 30; 30; 14; 8.5 pS for 1; 2; 3; 4, respectively. These values are similar to values found earlier for silica [10, 14]. All curves were calculated using the liquid and salt properties in [15].
6.4 The Salt Concentration and Channel Height Dependence

(a) $S_{str}$ (pA/bar)

(b) $1/R_{ch}$ (nS)

(c) $P_{max}$ (pW)

(d) $\varepsilon_{max}$ (%)

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Channel Height (nm)</th>
</tr>
</thead>
</table>
| 1 KCl, 490nm | same
| 2 LiCl, 490nm | channel
| 3 KCl, 490nm | channel
| 4 KCl, 75nm  | channel

Salt Concentration (M)
Chapter 6: Experiments on Electrokinetic Power Generation

<table>
<thead>
<tr>
<th>$h$ (nm)</th>
<th>$S_{str}$ (pA/bar)</th>
<th>$1/R_{ch}$ (nS)</th>
<th>$P_{max}$ (pW)</th>
<th>$\mathcal{E}_{max}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>75</td>
<td>2.2 ± 0.3</td>
<td>11 ± 2</td>
<td>1.7 ± 0.3</td>
<td>2.8 ± 0.5</td>
</tr>
<tr>
<td>490</td>
<td>34 ± 3</td>
<td>26 ± 7</td>
<td>190 ± 60</td>
<td>1.1 ± 0.4</td>
</tr>
</tbody>
</table>

Table 6.1: Channel height dependence of $S_{str}$, $1/R_{ch}$, $P_{max}$ and $\mathcal{E}_{max}$ (mean ± standard deviation) for the regime of maximum efficiency (low $n$) [16]. In this regime, the Stern conductance dominates the channel conductance ($G_{Stern} \approx \frac{1}{R_{ch}}$). 8 channels of $h = 75$ nm, and 13 channels of $h = 490$ nm were measured.

Predictions of the salt dependence of $S_{str}$ and $R_{ch}$, based on the exact PB-solution for the diffuse layer in a slit-like geometry, are strongly affected by the electrical properties of the channel walls (insets Fig. 6.3). A constant $\zeta$ fails to describe the salt dependence of either $S_{str}$ or $R_{ch}$ (dotted lines). A constant $\sigma = -8.2$ mC/m² describes $R_{ch}$ accurately, but overestimates $S_{str}$ (dashed curves), whereas a chemically varying $\sigma$, where $\sigma$ increases as function of $n$ due to the chemical equilibrium of the charge determining silanol groups at the silica surface [13], describes $S_{str}$ well, but underestimates $1/R_{ch}$ (dash-dotted curves). All the above boundary conditions result in an overestimate of $\mathcal{E}_{max}$ (inset Fig. 6.3d). No single boundary condition for the diffuse layer simultaneously describes the salt dependence of both $S_{str}$ and $R_{ch}$ accurately.

6.5 Stern Conductance

Our measurements can be well explained, however, if we consider the presence of a finite Stern layer conductance, $G_{Stern}$, at the surface. Mobile ions that are confined to the Stern layer (the first molecular layers adjacent to a charged surface) will contribute to the channel conductance without affecting the streaming conductance since Stern layer ions are presumed to move below the no-slip plane [17–19]. $G_{Stern}$ depends on the mobility and density of ions in the Stern layer, for which several microscopic models exist with significantly varying predictions [20]. Surface properties such as the roughness, charge density and chemical composition are also known to affect $G_{Stern}$ [21]. Our simultaneous measurements of $S_{str}$ and $R_{ch}$ in silica nanochannels, as well as our results for $P_{max}$ and $\mathcal{E}_{max}$, are well described by a chemically varying $\sigma$ for the diffuse layer with the addition of a constant $G_{Stern}$ (thick solid lines in Fig. 6.3). For our channels, we find values for $G_{Stern}$ in the range of $10 - 30$ pS.

The presence of a finite Stern conductance provides an additional pathway for power dissipation, thereby reducing the maximum efficiency predicted by theoretical calculations that ignored Stern conductance [5]. Moreover, the Stern...
conductance cancels the predicted height and ion mobility dependence of $E_{\text{max}}$ in the low salt regime, because $G_{\text{Stern}}$ dominates the channel conductance for low $n$. For the smaller $h = 75$ nm channels, $G_{\text{Stern}}$ was 2.4 times lower and $E_{\text{max}}$ was 2.5 times higher (Table 6.1). This lower Stern conductance could be rooted in the fabrication process, as the shorter etching may result in a lower surface roughness [22]. A systematic investigation of the microscopic origins of the Stern conductance should provide insight into how it can be minimized, which is crucial for improving the efficiency in future energy conversion experiments. Our electrokinetic method provides a sensitive tool to conduct such studies.

The fact that the Stern conductance barely changed when Li$^+$ replaced K$^+$ in the same channel for low $n$ [12] is quite remarkable, because their bulk mobilities differ by a factor of 2. The similarity of $G_{\text{Stern}}$ for K$^+$ and Li$^+$ counterions suggests that protons dominate the Stern conductance. Conduction by protons can be very efficient through the mechanism of hopping between water molecules [23]. Indeed, it has already been suggested that protons are mobile, and K$^+$ and Li$^+$ immobile in the Stern layer at the silica surface [19].

6.6 Conclusions

In conclusion, we have obtained the first measurements of electrokinetic power generation in individual nanofluidic channels. The data are excellently described by characterizing the fluidic device through its linear electrokinetic response properties. Our analysis of the efficiency reveals two distinct salt-regimes: the efficiency is highest at low salt when double layers overlap, and drops at higher salt. This is well described by modeling the diffuse layer boundary by a chemically varying surface charge and invoking a Stern layer conductance. The Stern conductance was found to be almost the same for counterions with very different bulk mobilities, suggesting that protons dominate the Stern conductance on silica. The highest efficiency of 3.2% was found for the smallest 75-nm high channel. Reducing the Stern conductance would further improve the efficiency, and should be the prime focus of future experimental work.

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References


The Poisson-Nernst-Planck equations govern the distribution of ions in a fluidic channel, which reduce to the PB equation for a system in thermodynamic equilibrium. Typical non-equilibrium effects, which are generally nonlinear, can occur at the channel entrance [6]. Nonlinear entrance effects were not observed in our nanochannels, which are very long. We thus may use PB theory, which provides convenient analytical expressions and linear electrokinetic responses [5].

These predictions hold for an optimized $R_L$. The $h$ and mobility dependence assume strong double layer overlap, and a value for $\sigma$ in the range $0.2 \lesssim h\sigma \lesssim 2\text{ nm} \times \text{C/m}$.

For measurements at low salt, $n \leq 10^{-4}$ M, $S_{str}$ and $R_{ch}$ exhibited a slow drift of typically a few percent per hour, resulting in scatter in the data. This drift can be attributed to a changing $\sigma$ due to aging [24] or a drifting pH. The independently measured bulk conductivity of the solution corresponded to tabulated values down to $n = 10^{-4.5}$ M [25]. For lower $n$, protons from dissociated water molecules enhance the conductivity. In nanochannels, $1/R_{ch}$ starts to deviate from bulk values already below $n = 10^{-3}$ M (Fig. 6.3b) due to the counterions in the double layer.

We found in three separate measurements that $1/R_{ch}$ was only $13 \pm 17\%$ higher for $10^{-4.5}$ KCl relative to $10^{-4.5}$ LiCl, while the limiting ionic conductivity of $K^+$ ions is about $90\%$ higher. For $n = 10^{-4.5}$, $G_{\text{Stern}} \approx 1/R_{ch}$ and the bulk conductivity is still well defined by the salt ions [11].

We used temperature $T = 296.15$ K; dielectrical constant $\epsilon = 79$; salt-corrected viscosities $\eta_{KCl} = \eta_{\text{water}}(1 - 0.01n)$ and $\eta_{LiCl} = \eta_{\text{water}}(1 + 0.148n)$,
with $\eta_{\text{water}} = 0.93$ mPas; ion mobility $\mu = \frac{\lambda^0}{F}$, with Faraday constant $F$, limiting equivalent conductivities $\lambda^0 = 7.06$ (K$^+$), $3.72$ (Li$^+$) and $7.33 \times 10^{-3}$ Sm$^2$mol$^{-1}$ [L. Coury, Curr. Sep. 18, 3 (1999)] and salt correction factors $\gamma_{KCl} = 0.727 + 0.031e^{-n/0.0012} + 0.082e^{-n/0.033} + 0.16e^{-n/0.47}$ and $\gamma_{LiCl} = 0.585 + 0.035e^{-n/0.0013} + 0.090e^{-n/0.034} + 0.29e^{-n/0.54}$, found by fitting tabulated values [25].

[16] Upon initially filling the $h = 75$ nm channels, $S_{str}$ was often very low ($< 0.5$ pA/bar) for hours. Over time, $S_{str}$ creeped to stable values of $\sim 2$ pA/bar.


[22] A rough surface can increase the thickness of the stagnant layer and the number of surface charges exposed to the liquid [21].


Chapter 7

Pressure-Driven Transport of Confined DNA Polymers in Fluidic Channels

The pressure-driven transport of individual DNA molecules in 175-nm to 3.8-μm high silica channels was studied by fluorescence microscopy. Two distinct transport regimes were observed: The pressure-driven mobility of DNA increased with molecular length in channels higher than a few times the molecular radius of gyration, whereas DNA mobility was practically independent of molecular length in thin channels. In addition, both the Taylor dispersion and the self-diffusion of DNA molecules decreased significantly in confined channels in accordance with scaling relationships. These transport properties, which reflect the statistical nature of DNA polymer coils, may be of interest in the development of "lab-on-a-chip" technologies.

7.1 Introduction

Transport of DNA and proteins within micro- and nanofluidic channels is of central importance to “lab-on-a-chip” bioanalysis technology. As the size of fluidic devices shrinks, a new regime is encountered where critical device dimensions approach the molecular scale. The properties of polymers like DNA often depart significantly from bulk behavior in such systems because statistical properties or finite molecular size effects can dominate there. DNA confinement effects have been exploited in novel diagnostic applications such as artificial gels [1], entropic trap arrays [2], and solid-state nanopores [3, 4]. These advances underline the importance of exploring the fundamental behavior of flexible polymers in fluid flows and channels [5–10] that underlie current and future fluidic technologies.

Most transport in micro- and nanofluidic separation applications is currently driven by electrokinetic mechanisms that result in a uniform velocity profile and low dispersion [11, 12]. An applied pressure gradient, in contrast, generates a parabolic fluid velocity profile that is maximal in the channel center and zero at the walls. Many important aspects of pressure-driven flows as a transport mechanism remain unexplored despite their ease of implementation and their ubiquity in conventional chemical analysis techniques such as high-pressure liquid chromatography. Our understanding of an object’s fundamental transport properties in parabolic flows - mobility and dispersion - is at present based mainly on models for rigid particles [13, 14] that explain several important effects such as: (i) hydrodynamic chromatography, the tendency of large particles to move faster than small particles because large particles are more strongly confined to the centre of a channel, where the flow speeds are highest, and (ii) Taylor dispersion [15], the mechanism by which analyte molecules are hydrodynamically dispersed as they explore different velocity streamlines by diffusion, an effect that has discouraged the use of pressure-driven flows in microfluidic separation technology. The applicability of rigid-particle models as useful approximations to the transport of flexible polymers is dubious in the regime where the channel size is comparable to the characteristic molecular coil size, the radius of gyration ($R_g$), yet remains untested there.

In this article, we present an investigation of the pressure-driven mobility and dispersion of individual DNA molecules in micro- and nanofluidic channels that reveals how this behavior is rooted in the statistical properties of polymer coils. DNA mobility exhibits both length-dependent and length-independent regimes, while both the Taylor dispersion and the self-diffusion of DNA are observed to be strongly reduced in confined channels, in accordance with scaling relationships.
7.2 Materials and Methods

Micro- and nanofluidic channels were prepared using a sodium silicate bonding procedure [16]. The 50-μm-wide and 4-mm-long channels were connected to large access holes at either end. The channel height, \( h \), ranged from 175 nm to 3.8 μm. The channels were filled with buffer solution by capillarity, and then electrophoretically cleaned of ionic impurities by applying 50 V across the channel for \( \sim 10 \) min. A DNA solution was introduced into the channels via the access holes, which were then connected to open fluid reservoirs (10-ml glass syringe bodies) via Peek tubing, all filled with bubble-free buffer solution. The fluorescently labeled DNA molecules were imaged with an electron multiplication CCD camera (Andor, Belfast, Ireland) at a rate of 5 Hz using an inverted oil-immersion fluorescence microscope (X100, 1.4 N.A.; Olympus, Tokyo, Japan) focused at the channel midplane.

The trajectories of DNA molecules were determined using custom-developed molecular tracking software (Matlab; Mathworks, Natick, MA) that locates a molecule’s center of mass as the first moment of the intensity distribution and follows it over a series of images. The integrated fluorescence intensity and the second moment of the intensity distribution (an estimate of \( R_g \)) were also calculated for each molecule, and used as criteria to filter imaging noise, damaged DNA fragments, or overlapping molecules. Molecular trajectories were verified by eye to ensure faithful tracking. Ambiguous molecular trajectories that would intersect, divide (break), or irreversibly stick to the channel were manually excluded.

The three linear DNA fragments studied were: 48,502-bp, unmethylated λ-phage DNA (λ-DNA; Promega, Leiden, The Netherlands); a 20,262-bp pBlue-script 2x Topo plasmid construct (Stratagene, La Jolla, CA); and an 8,778-bp pBluescript+ 1,2,4 λ-DNA fragment plasmid construct (Stratagene). The DNA fragments were fluorescently labeled with YOYO-1 dye (Molecular Probes, Eugene, OR) using a base pair to dye ratio of 6:1, and suspended in an aqueous solution containing 50 mM NaCl, 10 mM Tris, 1 mM EDTA (pH 8.0), and 2% 2-mercaptoethanol by volume to minimize photobleaching. The concentration of DNA molecules was adjusted to introduce a convenient density (\( \sim 1 – 20 \) in an 80-μm-wide field of view) into each fluidic device tested.
7.3 DNA Velocity in Confined Fluidic Channels

Micro- and nanofluidic channels (illustrated in Fig. 7.1A and 7.1B) were filled with aqueous buffer containing fluorescently labeled DNA molecules that were imaged by epifluorescence video microscopy. The three types of linear DNA fragment studied had lengths, \( L \), of 48.5 kbp (22 \( \mu \text{m} \)), 20.3 kbp (9.2 \( \mu \text{m} \)), and 8.8 kbp (4 \( \mu \text{m} \)). The corresponding equilibrium DNA coil sizes \([17]\) \( (R_g = 0.73, 0.46, \text{and } 0.29 \mu \text{m}, \text{respectively}) \) lie within the 175 nm to 3.8 \( \mu \text{m} \) range of the channel height, \( h \). DNA molecules were transported along the channel by means of an applied pressure gradient, \( p \), that was controlled by adjusting the height difference between two fluidic reservoirs connected to either end of the channel. The condition \( p = 0 \) was established by eliminating the drift of a collection of molecules. The pressure-driven fluid flow profile in a slit-like channel has been treated in detail and is characterized by a parabolic, Poiseuille flow across the channel height and a plug-like flow in the wide, transverse direction, decreasing to zero within a distance \( h \) of the slit edges \([18]\). Since \( h \) is much smaller than the 50 – \( \mu \text{m} \) channel width in our experiments, the fluid velocity as a function of the height, \( z \), from the channel midplane, \( U(z) \), is well approximated by the parabolic flow profile for a fluid between parallel plates,

\[
U(z) = \frac{h^2 p}{8\eta} \left(1 - \frac{4z^2}{h^2}\right), \tag{7.1}
\]

where \( \eta \) is the fluid viscosity. The trajectories of a large number of identical molecules were recorded for a series of \( p \) in each channel \([19]\). The fluid temperature, \( T \), was monitored to correct for viscosity variations.

The trajectory of each DNA molecule’s center of mass was tracked over a series of images using custom-developed software, as shown in Fig. 7.1C and D. The average velocity of a molecular ensemble along the direction of flow, \( \bar{V} \), was calculated to be the mean of the instantaneous center-of-mass velocities for all molecules of a given length in each channel, and at each \( p \). The axial dispersion caused by velocity fluctuations within the ensemble (illustrated in Fig. 7.1E) was parameterized by the dispersion coefficient, \( D^* \), which is defined by \( \langle (\Delta x - \bar{V} \Delta t)^2 \rangle = 2D^* \Delta t \), where \( \langle (\Delta x - \bar{V} \Delta t)^2 \rangle \) is the mean square displacement of a molecule from its mean-velocity-shifted center of mass position in the time interval \( \Delta t \). At \( p = 0 \), dispersion results only from the thermal self-diffusion of molecules, whose diffusion coefficient we denote \( D_0 \). Note that this situation represents DNA self-diffusion in a channel of height \( h \), and therefore includes hydrodynamic interactions with the walls and molecular confinement effects that are absent in bulk self-diffusion, whose coefficient we denote \( D_{\text{bulk}} \).
$\bar{V}$ increased linearly with $p$ for all DNA lengths in all channels. We found that $\bar{V}$ was between the calculated maximum velocity of the fluid in the channel, $U_{max} = \frac{h^3 p}{8 \eta}$, and the average fluid velocity, $\bar{U} = \frac{2}{3}U_{max}$ (Fig. 7.2A, inset). To compare the transport of DNA in fluid of constant $\eta$, we first corrected for small temperature variations by rescaling velocities as [20]

$$\bar{V} = \bar{V}(20^\circ C) = \frac{\eta(T)}{\eta(20^\circ C)} \bar{V}(T).$$

(7.2)

We then defined the pressure-driven DNA mobility, $\nu$, as the slope of $\bar{V}$ versus $p$, i.e., $\bar{V} = \nu p$. The standard deviation in the slope was taken to be the uncertainty in $\nu$. The dependence of pressure-driven transport on DNA fragment length is best revealed by comparing the relative values of $\nu$ that were measured for each DNA length in the same channel, and are therefore insensitive to microscopic...

Figure 7.1: Experimental observation of pressure-driven DNA transport in micro- and nano-fluidic channels. Schematic illustrations of (A) a rectangular, 50 – μm-wide, 4-mm-long silica fluidic channel and (B) the channel cross-section over which an applied pressure gradient generates a parabolic fluid velocity profile. (C) Imaging a fluorescently labeled 48.5-kbp DNA molecule as it was transported through an $h = 250$ nm channel by an applied pressure gradient of $1.44 \times 10^5$ Pa/m. The red dots indicate the center-of-mass positions, recorded at a rate of 5 Hz. (D) The molecular trajectory along ($x$ direction) and perpendicular to ($y$ direction) the fluid flow, as a function of time. The linear increase in $x$ position over time indicates a well-defined average pressure-driven velocity. No net velocity is observed in the $y$ direction. (E) The $x$ and $y$ components of the instantaneous molecular velocity as a function of time. The fluctuations along the flow are analyzed to study Taylor dispersion. The $y$ direction fluctuations are independent of applied pressure, and reflect thermal self-diffusion alone.
Figure 7.2: Dependence of pressure-driven DNA mobility on molecular length and channel height. (A) The average velocity of DNA molecules in an $h = 2.73 \, \mu m$ channel increases linearly with applied pressure gradient (inset). The slope of the curve defines the pressure-driven mobility, $\nu$, which is observed to lie between the expected peak and average fluid mobility in the channel. The mobility ratio $\nu/\nu_\lambda$ for 8.8- and 20.3-kbp-long DNA molecules, where $\nu_\lambda$ corresponds to 48.5-kbp-long $\lambda$-DNA molecules, is plotted as a function of the channel height. The solid lines indicate predictions of a transport model based on the equilibrium random-flight statistical behavior of DNA coils in a parabolic flow profile, as described in the text. Caption continued on next page.
7.4 The Statistical Polymer Distribution Model

The observed pressure-driven mobility behavior can be explained by the statistical distribution of DNA molecules modeled using equilibrium random-flight statistics in the limit of low fluid shear rates. This approach therefore departs from naïve conventional models that approximate polymer coils as rigid objects [13, 14]. We instead take the center-of-mass velocity of the DNA to be the average velocity of its segments, which travel at the local fluid velocity. $V$ can thus be expressed in terms of the average DNA segment concentration, $\rho(z)$, and $U(z)$, as

$$V = \int_{-h/2}^{h/2} \rho(z)U(z)dz / \int_{-h/2}^{h/2} \rho(z)dz. \quad (7.3)$$

Consequently, the problem of determining the relative molecular speeds is reduced to determining $\rho(z)$ as a function of $h$ and DNA length.

We model a polymer coil as a random flight whose equilibrium conformation is described by the Edwards diffusion equation in a uniform potential field [21],

Figure 7.2 (continued): (B) A schematic illustration of DNA configurations in a wide channel, in which DNA mobility increases with molecular length. A molecule’s center of mass is excluded from a region of length $\sim R_g$ from the channel wall, inducing large molecules to spend a greater amount of time in the central, high-velocity region of the fluid flow. (C) The length-dependent DNA density profiles predicted in an $h = 3.81 \mu m$ channel, with the parabolic fluid velocity profile indicated as a dashed line. (D) A schematic illustration of DNA configurations in a narrow channel, in which DNA mobility is independent of length. (E) The length-independent DNA density profile predicted for all three molecular lengths in an $h = 500 \text{ nm}$ channel, with the parabolic fluid velocity profile indicated as a dashed line.
\[ \frac{b^2}{6} \nabla^2 P(z, s) = \frac{b \partial P(z, s)}{\partial s}, \quad (7.4) \]

where \( P(z, s) \) is the probability that paths of contour length \( s \) end at \( z \), and \( b \) is the mean independent step size, called the Kuhn length. The average concentration profile of DNA segments, \( \rho(z) \), for a molecule of length \( L \) is given by \( \rho(z) = \frac{1}{L} \int_0^L P(z, s) P(z, L - s) \, ds \). The confinement of such a polymer to a narrow slit was first treated theoretically by Casassa \[21, 22\] by imposing noninteracting boundary conditions at the walls, setting \( P(\pm h/2) = 0 \). We have used Casassa’s exact result,

\[ P(z, s) = \frac{4}{\pi} \sum_{m=0}^{\infty} \frac{1}{2m+1} \exp \left( -\frac{(2m+1)^2 \pi^2 bs}{6h^2} \right) \cos \left( \frac{(2m+1)\pi z}{h} \right), \quad (7.5) \]

with \( b = 100 \text{ nm} \) to numerically evaluate solutions to Eq. 7.3. The predicted ratios of \( \nu \) for the three DNA lengths tested are plotted as solid lines in Fig. 7.2A.

Our polymer transport model predicts the length dependence of \( \nu \) well over the full range of channel heights studied: A length-independent transport regime is predicted for thin channels, as well as length-dependent transport for sufficiently large channels. The predicted cross-over between these regimes agrees with our observations. In the length-dependent regime, the predicted reduction in \( \nu/\nu_\lambda \) corresponds perfectly to our data for the 20.3-kbp DNA, and is only somewhat underestimated for the 8.8-kbp DNA in the highest channels. Note that our model contains no fitting parameters, relying instead on the well-established bulk radii of gyration for DNA to parameterize their statistical behavior.

The physical origin of the two transport regimes is made clear by considering the channel size limits for which useful analytic approximations to \( \rho(z) \) exist \[23\]: In large channels compared to the polymer coil size \( (h > 4R_g, \text{illustrated in Fig. 7.2B}) \), we find \( \rho(z) \propto \tanh^2 \left( \frac{\sqrt{\pi |z| - h/2}}{2R_g} \right) \), where \( R_g = \sqrt{Lb/6} \) is the equilibrium radius of gyration. The DNA concentration profile is flat at the centre of the channel where molecules can diffuse freely, but is depleted in a region that extends \( \sim 2R_g \) from the walls (Fig. 7.2C). Long molecules are therefore more strongly confined to the central, high-velocity region of the flow than short ones, explaining the observed length-dependent DNA mobility. This “hydrodynamic chromatography” transport regime for polymers has been proposed as a practical means to achieve size separation of long DNA molecules in microchannels because the mean separation between lengths increases linearly with \( \Delta t \), whereas the width of a single-DNA-length distribution should only grow as \( \sqrt{\Delta t} \) because of dispersion \[13, 24–26\]. Our statistical polymer transport picture suggests that the observed velocity of a DNA molecule should approach the mean velocity on
a measurement timescale, $\tau$, that greatly exceeds both the diffusion time across the channel, i.e., $\tau \gg \frac{6\eta(h-2R_g)^2R_g}{k_BT}$, as well as the longest timescale for internal molecular reconfiguration, known as the Zimm time, i.e., $\tau \gg \frac{0.4\eta R_g^3}{k_BT}$ [27].

Our model predicts an optimal channel height, $h \approx 10R_g$, for separating DNA molecules where $d\nu/dL$ is maximized. The resolving power of this technique would be limited in practice by constraints on a separation device’s length, injection mechanism, separation time, the resolution and the noise of DNA detection, among other considerations. A sensible comparison of DNA length separation by hydrodynamic chromatography to conventional technologies must therefore be made in the context of a complete device, which we do not attempt here.

In channels comparable to or smaller than the coil size ($h < 2R_g$, illustrated in Fig. 7.2D), we find $\rho(z) \propto \cos^2 \left( \frac{\pi z}{h} \right)$. In this situation, the lateral extent of a DNA molecule increases with length, but, importantly, its concentration profile across the channel height is length-independent (Fig. 7.2E), explaining why the $\nu$ are observed to be the same. This new “confined” transport regime is unique to flexible polymers, with no rigid-particle analog.

Our model successfully predicts pressure-driven DNA transport despite several assumptions that merit comment. We assume a constant $\eta$, as the influence of the polymers on the fluid viscosity is expected to be small for the low polymer concentrations and shear rates tested [28]. For sufficiently high shear rates relative to the molecular relaxation times, i.e., for high Weissenberg numbers, $Wi$, fluidic shear forces could potentially distort DNA conformations from their assumed equilibria. In all our experiments, $Wi$ was below 5, the onset of significant stretching in the flow direction [7]. In addition, fluidic shear is concentrated near the channel walls, where the DNA concentration is depleted. The model also neglects forces normal to the flow direction that may arise from hydrodynamic coupling of the polymer segments to the channel walls [29, 30] or from the fluid inertia itself [31]. Theory [32] and simulations [29, 30] predict that hydrodynamic interactions result in the migration of polymers towards the channel center to a degree that increases with $Wi$ and $h$, an effect that has been experimentally confirmed for 48.5-kbp DNA in very large ($h = 126 \mu m$) channels [33]. These effects are not expected to be significant for most of the range of small $h$ tested in our experiments, but their onset at the highest $Wi \sim 5$ and $h \sim 4 \mu m$ tested may explain the small discrepancy between our model predictions and the length-dependent $\nu/\nu_0$ observed there. Significant distortion of the equilibrium DNA concentration profile across the channel height by shear and hydrodynamic interactions, however, would result in a nonlinear $\nabla \nu$ versus $p$ curve, which was not observed.
7.5 DNA Dispersion in Confined Channels

DNA mobility in the low-pressure regime appears to be well explained by equilibrium polymer configurations. The dispersive behavior of DNA is of equal fundamental and practical significance, and depends on molecular conformation fluctuations. Fig. 7.3A shows the dependence of $D^*$ for 48.5-kbp DNA in high ($h = 2.73 \mu m$) and low ($h = 500 \text{ nm}$) channels on $V$. The Taylor dispersion of 48.5-kbp DNA was found to be greatly reduced in the thin, $h = 500 \text{ nm}$ channel relative to the $h = 2.73 \mu m$ channel. Taylor dispersion theory [34] predicts that $D^*$ can be expressed as the sum of a component originating entirely from molecular self-diffusion ($D_0$ in the present case) and a convective component that scales as $V^2$. For all $h$, the dispersion of DNA can indeed be seen to obey $D^* = D_0 + \alpha_T V^2$, where $\alpha_T$ is a fit parameter that we call the Taylor time because it quantifies the hydrodynamic component of Taylor dispersion, and is related to the time required for an object to explore all regions of the flow profile. The dependence of $\alpha_T$ on $h$ for all DNA lengths is plotted in Fig. 7.3B. A strong reduction in $\alpha_T$ was observed with decreasing $h$ for all but the smallest channels. For very small channels ($h \leq 250 \text{ nm}$), $\alpha_T$ increased as $h$ decreased, which we attribute to local fluid velocity variations caused by irregularities in the channel cross-section that gain increasing importance in the thinnest channels. $\alpha_T$ generally decreased with increasing DNA length. The nearly constant slope of $\alpha_T$ versus $h$ on the log-log scale of Fig. 7.3B for all DNA lengths suggests the power-law dependence $\alpha_T \propto h^2$ [35]. Linear fits of $\alpha_T$ to $h^2$, presented as solid lines in Fig. 7.3B, reveal that $\alpha_T/h^2$ decreased with $L$ as $\alpha_T/h^2 \propto L^{-0.46\pm0.04}$ (Fig. 7.3B, inset).

The observed dispersion of DNA in small channels is striking when compared to the predictions of existing Taylor dispersion theory (Fig. 7.3C). Axial dispersion in a parabolic flow profile was first treated by Taylor [15] for a slow-moving point-like solute in a circular tube. On long time scales compared to the time for a particle to diffuse across the channel height, a condition that is satisfied in our experiments, the dispersion coefficient of a point-like solute in a thin, rectangular channel is given by $D^* = D_0 + \alpha_T V^2$, where $\alpha_T = 0.038 \times h^2/D_0$ [36]. The point-particle model therefore captures the observed $\alpha_T \propto h^2$ behavior. However, it fails to predict two important aspects of the observed DNA dispersion: First, the model overestimates $\alpha_T$ by more than an order of magnitude for all $h$ when $D_0$ is taken to be the known bulk molecular diffusion constant. Second, the model predicts the opposite $\alpha_T$ length dependence to what is observed: For longer DNA, $D_0$ is smaller, and $\alpha_T$ should increase as molecules spend more time on the same fluidic streamline. In fact, $\alpha_T$ is observed to decrease with increasing
Figure 7.3: Taylor dispersion of DNA in micro- and nano-fluidic channels. (A) The dispersion coefficient of λ-DNA molecules is plotted as a function of average molecular velocity for \( h = 2.73 \, \mu m \) and \( h = 500 \, nm \). Solid lines indicate fits of \( D^* = D_0 + \alpha_T V^2 \). The Taylor time, \( \alpha_T \), quantifies the hydrodynamic component of dispersion. (B) The \( h \) dependence of \( \alpha_T \) is plotted for all DNA lengths. The \( \alpha_T \) values of the smallest two channels are likely dominated by irregularities in the channel cross-section, and are consequently indicated with open symbols and excluded from further consideration. The data are well described by the power-law scaling relation, \( \alpha_T \propto h^2 \), which is fit for each DNA length and plotted with the solid lines. The fits provide a measure of the length dependence of Taylor dispersion through the average value of \( \alpha_T/h^2 \), which is found to decrease as \( L^{-0.46 \pm 0.04} \) (inset). (C) The observed values of \( \alpha_T \) for the 8.8-kbp DNA are compared to point-like and rigid-particle models of Taylor dispersion, highlighting the inadequacy of existing theories for describing the dispersion of polymers in confined channels. (D) Upon plotting \( \alpha_T \) versus \( h^2/R_g \), we obtain a unique curve for all DNA lengths, suggesting a scaling relationship for DNA Taylor dispersion in small channels. The curve is linear in the thin channel limit \( (h^2/R_g \leq 1 \, \mu m) \) with a slope of \( 1.09 \pm 0.11 \), and departs from this power-law scaling at higher \( h^2/R_g \).
DNA length.

Models approximating DNA behavior by rigid-particle dispersion also fail to describe the observed behavior of DNA in micro- and nanofluidic channels. In the simplest model, a polymer coil is treated as a free-draining, rigid sphere whose diameter is \(6R_g/\sqrt{\pi}\) \[13\]. Since the sphere cannot explore all streamlines equally, the \(h\) dependence of \(\alpha_T\) becomes modified relative to the point particle model as \(\alpha_T \propto h^2 \rightarrow \alpha_T \propto h^2 (1 - 6R_g/h\sqrt{\pi})^6\). The predictions of this rigid-particle model, which are plotted for 8.8-kbp DNA in Fig. 7.3C, overestimate \(\alpha_T\) in high channels and predict that \(\alpha_T\) should vanish as \(h\) approaches the sphere diameter, which is clearly not observed. More elaborate rigid-particle models that include hydrodynamic interactions \[14\] or particle size fluctuations \[37\] do not resolve these glaring inconsistencies. An analytical treatment of many interacting Brownian particles \[38\] is not tractable for large polymers, and computer simulations of polymer Taylor dispersion are lacking.

A heuristic description of DNA Taylor dispersion in micro- and nanofluidic channels is suggested by the observed \(L\) and \(h\) dependence of \(\alpha_T\). In Fig. 7.3D, \(\alpha_T\) is plotted as a function of \(h^2/\sqrt{L}\) for all DNA lengths. Remarkably, we find that all points appear to lie on a common curve over two decades, with a slope of \(1.09 \pm 0.11\) in the thin channel limit \((h^2/\sqrt{L} \leq 2 \, \mu m^{3/2})\), and with the data departing from the straight line at higher \(h^2/\sqrt{L}\). Although DNA is an extended statistical object, the convective component of DNA dispersion in thin micro- and nanofluidic channels is consistent with a point-like solute description, i.e., \(\alpha_T = 0.038 \times h^2/D_{eff}\), where the effective DNA diffusion coefficient, \(D_{eff}\), scales as \(D_{eff} \propto \sqrt{L}\). From the fit to our data, we find \(D_{eff} \approx 9.9 \, \mu m^{3/2} s^{-1} \times \sqrt{L}\). This result is in stark contrast to the bulk diffusion constant, \(D_{bulk}\), which is known to obey \(D_{bulk} = 4.5 \, \mu m^2 s^{-1} \times L(\mu m)^{-0.611} \ [17]\). \(D_{eff}\) therefore exceeds \(D_{bulk}\) for molecules larger than \(L \approx 490\, nm\), a value corresponding to only a few DNA Kuhn segments. The surprising dispersion properties of DNA in small channels beg the development of a microscopic model. Flexible polymers differ crucially from point-like or rigid particles in that they possess many internal degrees of freedom. These may enable DNA to explore the parabolic flow more effectively, leading to an enhanced apparent diffusivity. These are also at the root of entropic elasticity \[39\], which would tend to confine the molecular center of mass to the center of the channel, thereby suppressing Taylor dispersion relative to that of point particles, while permitting fluctuations absent in rigid-particle models.

The high effective diffusion coefficient that can account for the reduced hydrodynamic dispersion of DNA in small channels is not caused by a high centre of mass self-diffusion. Indeed \(D_0\) is a measure of molecular self-diffusion, and was found to decrease with decreasing \(h\) (Fig. 7.4). At low \(R_g/h\), the ratio \(D_0/D_{bulk}\)
was nearly 1, and it decayed slowly with $R_g/h$ for $R_g/h \geq 0.1$. Above $R_g/h \approx 0.5$, the self-diffusion of DNA decreased rapidly as $D_0 / D_{\text{bulk}} \propto (R_g/h)^{-2/3}$. This scaling relationship was predicted by de Gennes [40] for sufficiently small channels in which highly confined molecules expand laterally, leading to a higher viscous drag and hence a reduced self-diffusion coefficient. First confirmed experimentally in a narrow tube geometry [41], this behavior has been modeled by computer simulations and experimentally verified for $R_g/h$ as high as 1 in a slit geometry [29, 42]. Here we see that $D_0 / D_{\text{bulk}} \propto (R_g/h)^{-2/3}$ to $R_g/h$ values as high as 7 [43].

7.6 Conclusions

In conclusion, we have shown how the pressure-driven transport behavior of DNA molecules in micro- and nanofluidic channels is dominated by the statistical properties of polymer coils. The distribution of a random-flight polymer across a channel leads to a pressure-driven mobility that increases with molecular length in large channels, and remains independent of length in channels that are small
compared to molecular coil size. The Taylor dispersion of DNA molecules is highly suppressed in confined channels, and decays with channel height and molecular length according to a power-law scaling relationship. These polymer transport properties are of considerable significance to bioanalysis technology aimed at the separation of DNA by length or the uniform transport of DNA molecules through a fluidic system. An understanding of DNA transport characteristics can therefore guide the design of fluidic channels, the fundamental components of lab-on-a-chip technology.

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References

The pressure gradients tested were limited by the $\sim 80 \, \mu m/s$ maximum molecular velocity to be reliably observable, and by the maximum pressure gradient generated by an 80-cm-high fluid column.

The temperature-dependent value of $\eta$ was parameterized by $1.05 \times 10^{-3} \, \text{Pa}\cdot\text{s} \times 10^{(1.3272 \times (20-T)-0.01053 \times (20-T)^2)/(105+T)}$, which was obtained by fitting the temperature dependence of water’s viscosity [44] and rescaling the absolute viscosity based on a measurement of the buffer solution viscosity using a viscometer (Low Shear 40; Contraves, Zürich, Switzerland). We calculated $p$ as $gH\varrho/l$, where $g$ is the acceleration due to gravity (9.81 m/s$^2$), $\varrho$ is the buffer density (1 g/ml), $H$ is the fluid column height, and $l$ is the effective channel length (4.08 mm) that includes entrance effects.


[35] The fit slopes were found to be $1.81 \pm 0.26$, $1.94 \pm 0.20$, and $1.60 \pm 0.16$ for the 48.5-, 20.3-, and 8.8-kbp fragments, respectively.


[43] An additional $h = 107$ nm channel was used to test the scaling of $D_0$ to high degrees of confinement.

Summary

We report measurements on the pressure-driven transport of fluids and DNA polymers through nanochannels in previously unexplored regimes of confinement, where double layers overlap and DNA is significantly squeezed. In such small fluidic geometries, fundamentally new separation and detection mechanisms become available. Chapter 1 gives an overview of the important new science and novel applications that can be expected when shrinking the dimensions of fluidic systems into the nano regime. Chapter 2 provides the theoretical background for the experiments which are described in the rest of this thesis.

In Chapter 3 we report our measurements on the pressure-driven transport of simple monovalent salt solutions through individual rectangular nanochannels made of fused silica. This material acquires a negative charge when it is brought into contact with an aqueous solution due to the dissociation of protons. The negative surface charge is screened by positive counterions in the double layer. The counterions are carried with the pressure-driven fluid flow along the surface, generating an electrical current which was measured. We found an increase of this so-called streaming current as function of the channel height, which is explained by the higher fluid velocity in the double layer for larger channels. The streaming current decreased as function of salt concentration, caused by the reduced average speed of the counterions which are located closer to the surface at high salt due to a thin double layer. An effective surface charge density can be calculated from the measurements of the streaming currents, by modeling the fluid speed as a parabolic Poiseuille flow with zero velocity at the walls, and modeling the ion distributions with the Poisson-Boltzmann equation. We find that the surface charge of silica increases as function of salt concentration. This finding corresponds excellently to the chemical equilibrium model of protons reacting with the charge determining silanol groups at the surface. Our results highlight the appropriate boundary conditions when considering electrokinetic effects in silica channels, such as electro-osmotic flows.
Our measurements of the streaming current in the presence of multivalent counterions are presented in Chapter 4. Multivalent counterions can cause the effective surface charge to flip sign, an effect known as charge inversion. This counterintuitive effect results from the strong electrostatic interactions of the multivalent ions with the surface (attractive) and between themselves (repulsive), which causes the ordering of multivalent ions into a structure reminiscent of a two-dimensional crystal. This so-called strongly correlated liquid is accompanied by a lowering of the free energy and the binding of additional counterions to maintain thermodynamical equilibrium. Charge inversion occurs when enough of these additional counterions bind to the surface. We report the first measurements of charge inversion at high ionic strength, where streaming currents are still a sensitive probe while other methods fail. We found that divalent ions cause charge inversion of the silica surface, but only at very high concentrations. Charge inversion occurs at much lower concentrations for trivalent ions. Adding monovalent salt to solutions contained trivalent ions was found to cancel charge inversion. This effect was modeled within the framework of the strongly correlated liquid theory when the entropy of mixing was included. According to this model, the charge inversion disappears at high salt because the binding energy due to the correlations is strongly reduced by screening. The free energy is then dominated by the entropy of mixing, which causes the density of multivalent ions at the surface to decrease.

Electrical energy is harvested from the fluidic system, when the pressure-driven streaming current is allowed to flow through an external load resistor. In such a system, hydrostatic energy is translated into electrical power. The efficiency of this energy conversion process was theoretically evaluated for slit-like channels in Chapter 5, using exact solutions for the fluid flow (Poiseuille with no-slip boundary conditions) and the ion distributions (Poisson-Boltzmann with a constant surface charge density). First, the generated fluid and ion flow in response to an applied pressure or potential difference are calculated. These linear responses represent the elements in an equivalent circuit, from which we can calculate the efficiency. The highest efficiency is found to occur in the regime of strong double-layer overlap, i.e. at low salt concentrations in nanoscale fluidic channels. In this regime, co-ions are electrostatically repelled from the nanochannel, reducing power dissipation by electrical conduction, while counterions are located relatively far from the channel walls, where they add strongly to the streaming current due to the large fluid speed. We present an exact analytical expression for the high efficiencies in this regime of strong overlap. The efficiency has a maximum as function of the product of the channel height and the surface charge, i.e. for each material we find an optimal channel height. Also, the efficiency is
found to decrease as function of the counterion mobility. We find a maximum theoretical efficiency of about 12% for lithium ions in water. Less common ions with lower mobilities could produce even higher efficiencies.

Our measurements on the efficiency of electrokinetic power generation in rectangular silica nanochannels are reported in Chapter 6. The response of the nanochannel connected to a load resistor corresponded excellently to the linear equivalent circuit model. To obtain the maximum power and efficiency, the load resistor must be similar to the channel resistance. To test the predictions of Chapter 5, we measured the energy conversion efficiency for an optimized load resistor as function of the salt concentration, channel height and counterion mobility. Conform our expectations, the highest power and efficiency occurred at low salt concentrations. The other theoretical predictions for the dependence on the channel height and ion mobility were not observed in the data, due to a large conductance of the Stern layer: Counterions in the thin Stern layer behind the no-slip plane do not move when a pressure difference is applied, but have a finite mobility in electrical fields. This so-called Stern conductance derives from a discrepancy in the electrical boundary conditions obtained from simultaneous measurements of the streaming current and the electrical conductance. At low salt concentrations, the Stern layer conductance is found to dominate the conductance of the nanochannel, and strongly reduces the efficiency by providing an additional pathway for power dissipation. Our electrokinetic method provides a new tool for the direct measurement of this Stern conductance. Remarkably, the Stern conductance on silica is found to be the same for counterions whose bulk mobilities differ by a factor of two. This observation can be explained if we assume that protons dominate the conductance in the Stern layer for silica. The highest efficiency of about 3% was found for a 75 nm high channel at low salt. This efficiency should be higher for materials with a lower Stern conductance.

The last chapter in this thesis contains our experimental study on the pressure-driven transport of DNA polymers in slit-like nanochannels. Two distinct transport regimes could be identified. When the channel is much larger than the size of the DNA, the DNA velocity is found to increase with the polymer length. A large polymer moves faster because its center-of-mass cannot probe the slow fluid velocities close to the channel walls. The velocity of strongly confined DNA was found to be independent of the DNA length. In this regime of strong confinement, the polymer assumes a pancake-like shape and the segment distribution across the channel height becomes independent of the polymer length. The polymer velocity is taken as the average speed of the segments, and is therefore independent of the polymer length. Our experimental results for the velocity of various DNA lengths in a wide range of confinement compared excellently to calculations,
using the freely jointed chain to model the DNA segment distribution without any fit parameters. Our experiments on the dispersion of DNA molecules in a pressure-driven flow could not be described by existing models. The dispersion of DNA was found to be lower compared to predictions for point-like particles. Moreover, DNA dispersion decreased as function of DNA length, in contrast to point-like particles where the dispersion should increases with the particle size. From our data, we constructed an empirical scaling relation for the Taylor dispersion of DNA in slit-like channels as function of the DNA length and the channel height. The self diffusion of DNA as function of the degree of confinement is found to scale exactly according to predictions by De Gennes for self-avoiding polymers. Our findings on the transport properties of polymers in nanochannels are of interest for on-chip bioanalysis technologies, where DNA molecules can be either separated by length, or co-transported through a fluidic system.

In conclusion, we have employed the relatively simple method of a pressure-driven flow through a rectangular nanofluidic channel to study a wide variety of subjects. The experimental work in this thesis contributes to our understanding of the double layer, the electrical surface properties of silica, the mechanisms of charge inversion, the possibilities and limitations of electrokinetic power generation, and the transport of DNA through nanochannels.

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December 2006
Samenvatting

Dit proefschrift beschrijft een aantal experimenten over het drukgedreven transport van vloeistoffen en DNA polymeren door nanokanaaltjes in het nieuwe regime van kleine afmetingen, waar de elektrische dubbellagen overlappen en DNA wordt samengedrukt. In zulke kleine geometrieën treden fundamenteel nieuwe scheidings- en detectie-mechanismen op. Hoofdstuk 1 geeft een overzicht van de belangrijkste nieuwe fysische effecten en innovatieve toepassingen die we mogen verwachten als we vloeistofsystemen verkleinen tot de nanoschaal. Hoofdstuk 2 beschrijft de theoretische achtergrond die in rest van dit proefschrift wordt toegepast voor de interpretatie van de experimenten.

In hoofdstuk 3 beschrijf ik onze metingen aan het pompen van monovalente zoutoplossingen door rechthoekige nanokanaaltjes, met een hoogte die veel kleiner is dan de breedte. Het siliciumoxide materiaal van de kanalen krijgt een negatieve lading als het in contact komt met een waterige oplossing door de dissociatie van protonen. De negatieve oppervlaktelading wordt afgeschermd door positieve tegen-ionen in de dubbellaag. Deze tegen-ionen worden meegevoerd met de drukgedreven vloeistofstroom, en genereren op deze wijze een electrische stroom die we kunnen meten. We vinden in onze experimenten dat deze zogenaamde vloeistroom toeneemt met de kanaalhoogte, hetgeen verklaard wordt door de grotere vloeistofsnelheid in de dubbellaag voor hogere kanalen. Een tweede effect dat we meten is een afname van de vloeistroom als functie van de zoutconcentratie. De reden hiervoor is dat bij hoog zout de dubbellaag aan het oppervlak dunner wordt, zodat de tegen-ionen gemiddeld dichter bij het oppervlak zitten waar de vloeistofsnelheid laag is. We kunnen een effectieve oppervlaktelading berekenen uit onze metingen van de vloeistroom, door de vloeistofsnelheid te modeleren als een Poiseuille stroming met een parabolisch profiel, en de ionenverdeling te berekenen met de Poisson-Boltzmann vergelijking. We vinden op deze manier dat de effectieve oppervlaktelading toeneemt als functie van de zoutconcentratie. Dit resultaat was zeer goed te beschrijven met een evenwichtsreactie tussen
protonen en silanolgroepen aan het oppervlak. Onze metingen geven het belang aan van het meenemen van de juiste elektrische oppervlakte eigenschappen bij het beschouwen van electrokinetische effecten in nanokanalen.


Als de vloeistroom door een externe weerstand wordt geleid kunnen we elektrische energie onttrekken aan de nanokanaaltjes. In zo’n systeem wordt hy drostatische energie omgezet in elektrische energie. De efficiëntie van dit conversieproces is theoretisch uitgewerkt in hoofdstuk 5, waarbij exacte oplossingen voor de vloeistofstroming en de ionenverdelingen zijn gebruikt. Eerst berekenen we de vloeistof- en ionenstroom door het kanaal als we een druk- of een potentiaalverschil aanleggen. Deze lineaire eigenschappen vormen de elementen van een electronisch equivalent circuit, waarmee we de efficiëntie eenvoudig kunnen berekenen. Het blijkt dat de efficiëntie het hoogst is als de dubbellagen sterk overlappen, oftewel bij lage zoutconcentraties in kanaaltjes met nanometer dimensies. In dit regime worden co-ionen door electrostatische interacties geweerd uit het kanaaltje, zodat het vermogensverlies door de geleiding van deze ionen wordt geminimaliseerd. Tevens zijn bij deze lage zoutconcentraties de tegen-ionen gemiddeld ver verwijderd van de wanden waar ze sterk bijdragen aan de opgewekte stroom door de hoge vloeistofsneldheid. Voor dit regime van overlappende dubbellagen hebben we een exacte formule voor de efficiëntie afgeleid. De effi-
ciëntie heeft een maximum als functie van het product van de kanaalhoogte en de oppervlakteelading, oftewel, voor elk materiaal met een bepaalde lading bestaat een optimale kanaalhoogte. Verder blijkt dat de efficiëntie toeneemt voor ionen met een lagere mobiliteit. De hoogste efficiëntie die we theoretisch kunnen bereiken in waterige oplossingen met veelvoorkomende ionen is ongeveer 12 procent, bij gebruik van lithium ionen. Er bestaan ionen met een nog lagere mobiliteit, en dus een nog hogere optimale efficiëntie.

We hebben de efficiëntie van electrokinetische energieopwekking ook experimenteel onderzocht zoals beschreven in hoofdstuk 6. Het gedrag van een nanokanaal verbonden met een externe weerstand blijkt goed beschreven te worden met het lineaire electronisch equivalentcircuit uit het vorige hoofdstuk. Om het elektrisch vermogen en de efficiëntie te optimaliseren moet de externe weerstand ongeveer gelijk zijn aan de weerstand van het nanokanaaltje zelf. Om de andere voorspellingen van de theorie te testen hebben we metingen verricht als functie van de zoutconcentratie, de kanaalhoogte en de mobiliteit van de tegen-ionen. Zoals verwacht zijn het vermogen en de efficiëntie het hoogst bij lage zoutconcentraties. De voorspelde afhankelijkheid van de kanaalhoogte en de ionenmobiliteit worden tenietgedaan door een behoorlijke oppervlaktegeleiding: De vloeistof en de ionen in een dunne laag aan het oppervlak, de Stern laag, bewegen niet mee met de drukgedreven vloeistofstroom in het kanaaltje, maar deze ionen kunnen wel bewegen onder invloed van een electrisch veld. Deze zogenaamde Stern geleiding kon nauwkeurig worden bepaald door onze gelijktijdige metingen van de vloeistroom en de geleiding van het nanokanaaltje met elkaar in overeenstemming te brengen. Uit onze metingen blijkt dat de Stern geleiding de totale geleiding van de kanaaltjes domineert bij lage zoutconcentraties. Deze extra geleiding zorgt voor een sterke verlaging van de efficiëntie door electrische dissipatie. De toegepaste electrokinetische meetmethode is een zeer geschikte manier om de Stern geleiding direct te meten. Tot onze verrassing vonden wij exact dezelfde Stern geleiding voor tegen-ionen met een zeer verschillende bulkmobiliteit. Dit opeenmorrelige resultaat is te verklaren door aan te nemen dat de Stern geleiding aan siliciumoxide oppervlakken gedomineerd wordt door protonen. De hoogste efficiëntie, ongeveer 3%, is gevonden voor een 75 nm kanaaltje en een lage zoutconcentratie. We verwachten dat deze efficiëntie aanzienlijk hoger kan zijn voor materialen met een lagere Stern geleiding.

Het laatste hoofdstuk beschrijft onze experimentele studie over het drukgedreven transport van DNA polymeren in de rechthoekige nanokanaaltjes. Twee fundamenteel verschillende transportregimes konden worden onderscheiden. Als het kanaal veel hoger is dan de grootte van een DNA molecuul, neemt de transportsnelheid toe met de moleculengrootte. De reden is dat het zwaartepunt van
de grote moleculen niet zo dicht bij de wand kan komen, waar de vloeistofsnellheid laag is. De grote moleculen bewegen dus gemiddeld sneller. In het tweede regime is het kanaal kleiner dan het DNA. We zien dan dat kleine en grote DNA moleculen even snel door het kanaal bewegen. In dit regime wordt de bolvormige evenwichtsconfiguratie van het DNA platgedrukt tot een soort pannekoekvorm, en de verdeling van de polymeersegmenten is dan onafhankelijk van de polymeergrootte. De transportsnelheid van het DNA is gedefinieerd als de gemiddelde snelheid van de segmenten, en deze hangt dan dus ook niet af van de DNA grootte. Onze meetresultaten in beide regimes zijn in overeenstemming met de bovenstaande beschrijvingen, waarbij we de segmentverdeling hebben berekend voor ideale polymeren zonder fit parameters. De gemeten dispersie van de DNA moleculen in een drukgedreven stroming konden niet in overeenstemming worden gebracht met bestaande modellen. De werkelijke DNA dispersie is kleiner dan de voorspellingen voor puntdeeltjes. Een nog belangrijker verschil is dat de gemeten DNA dispersie afneemt voor grotere moleculen, terwijl de modellen voor puntdeeltjes precies het omgekeerde voorspellen. Uit onze data hebben we een empirische relatie gedestilleerd, die de schaling van DNA dispersie in rechthoekige kanaaltjes accuraat beschrijft als functie van de kanaalhoogte en de DNA grootte. Tenslotte hebben we de diffusieconstante van de DNA moleculen gemeten bij verschillende kanaalhoogtes in de afwezigheid van een vloeistofstroom. De metingen kloppen precies met de schalingsrelatie van De Gennes voor niet-ideale polymeren. Onze bevindingen over de transporteigenschappen van polymeren in nanokanaaltjes zijn van belang voor on-chip bioanalyse technologieën, waar DNA moleculen afhankelijk van de behoefte gescheiden kunnen worden, maar ook gezamenlijk kunnen worden getransporteerd in een device.

Kort samengevat hebben we met het relatief eenvoudige systeem van een drukgedreven vloeistofstroom door een rechthoekig nanokanaaltje een uitgebreid scala aan onderwerpen bestudeerd. De experimentele resultaten in dit proefschrift dragen bij aan ons begrip over de opbouw van de dubbellaag, de oppervlakte-lading van silicium, de mechanismen van ladinginversie, de mogelijkheden en beperkingen van electrokinetische stroomopwekking, en het transport van DNA in nanokanaaltjes.

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List of Publications

1. *Power Generation by Pressure-Driven Transport of Ions in Nanofluidic Channels*

2. *Quasi-2D Electrokinetic Transport in Fluidic Channels*
   In preparation.

3. *Electrokinetic Energy Conversion Efficiency in Nanofluidic Channels*

4. *Pressure-Driven Transport of Confined DNA Polymers in Fluidic Channels*
   D. Stein, F.H.J. van der Heyden, W. Koopmans and C. Dekker.

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