Modelling Electroosmotic and Pressure-Driven Flow in Porous Media for Microfluidic Applications

by

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**A Thesis Submitted to the
Faculty of Graduate Studies and Research
in Partial Fulfillment of the Requirements for the Degree of**

Master of Applied Science (M.A.Sc.)

**Department of Electronics
Faculty of Engineering
Carleton University
Ottawa, Ontario
April, 2004**

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ABSTRACT

MODELLING ELECTROOSMOTIC AND PRESSURE-DRIVEN FLOW IN
POROUS MEDIA FOR MICROFLUIDIC APPLICATIONS

by Nathan Scales

ADVISOR: Dr. N. Tait

April, 2004

Ottawa, Ontario

In this work, a model is developed that provides a general framework for the modelling of electroosmotic and pressure-driven flow in porous media of different geometries, for use in microfluidic devices. This model is compatible with the standard models for flow in porous media, but incorporates viscous shear stresses as well, enabling the modelling of fluid flow in porous and open channels, or in channels in which the bounding walls have a different zeta potential than the porous material. Simple models for dispersion in porous media, due to the flow profile in individual pores, and due to a distribution of pore sizes in the material, are developed. Analytical solutions to the proposed model are provided for electroosmotic flow in a few simple geometries. Numerical solutions are then used to fit experimental data from the capillary electrochromatography literature, as well as the experimental results of two simple microfluidic devices.

Acknowledgments

I would like to thank my supervisor, Dr. Niall Tait, for his help and advice, and for his willingness to take on a project in a research area new to the Department of Electronics. I would also like to thank Dr. Imants Lauks for the inspiration of the thesis topic, and for a number of fruitful discussions that helped direct me in my research. I would like to thank Ray Pierce and Benoit Bergevin of Epocal for their technical support, their time, and the construction and testing of the microfluidic devices.

I would also like to thank my wife, Christine, for her continued support and encouragement throughout my research, and for her help in editing the thesis drafts.

Finally, I would like to thank the Ontario Graduate Scholarship Program, Epocal, and Carleton University for their financial support and for providing the resources necessary to conduct my research.

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Chapter 1

Introduction

1.1 Introduction to the Field

Recent advances in microfabrication technology are enabling researchers to miniaturize many of the tools commonly used for analysis in chemistry and biology today. Such miniaturization is expected to increase the speed of analysis, improve the resolution of the techniques, and reduce the amount of reagent required, as well as the cost of the devices themselves. It is becoming possible to perform many different chemical processes at a time on a single chip, allowing researchers to automate and coordinate different stages of analysis. Such devices have been dubbed *lab-on-a-chip* devices, as it is hoped that, literally, it will be possible to reproduce the functionality of entire laboratories on a single microchip. It is expected that this will revolutionize chemistry, biology, and medicine, much in the same way that the invention of the integrated transistor revolutionized the electronics industry.

As much of chemistry and biology requires contact with fluids, *microfluidics* (the practice of controlling fluids at very small scales) is thought by many to be essential in bringing about many of the developments required for lab-on-a-chip devices to reach their full potential. Due to the difficulties of fabrication at the microscale, microfluidic devices incorporating moving parts to direct the fluid often have reliability issues, and the high pressures required to force the fluid from region to region can exacerbate these problems. A method of directing fluids without moving parts is therefore of great interest to researchers in the field.

The possibility of using an electric field to control the fluid flow directly is therefore

Figure 1.1: Illustration of the anatomy of the double layer. Ions of opposite charge in the fluid will be attracted to the charged surface, forming a double layer that shields the rest of the channel from the wall potential. The charge density of ions will approach zero quickly away from the wall.

an enticing prospect for many researchers. Researchers frequently take advantage of a phenomenon known as *electroosmosis* to allow them to manipulate fluids using electric fields. If a solution is exposed to a medium with charged walls, ions of opposite charge in the solution will be attracted to the walls, forming what is called a *double layer* of charge. The concentration of charge will be high close to the wall, and will decrease rapidly away from the wall (see Figure 1.1). The application of an electric field parallel to the walls will force the ions close to the wall to move, inducing the fluid in the rest of the channel to move as well due to viscous drag (see Figure 1.2). The direction of motion depends upon the sign of the ions near the wall, which in turn depends upon the sign of the charge on the wall.

Electrophoresis is the movement of charged molecules in a fluid due to an applied electric field. The direction of electrophoresis is dependent upon the sign of the charged molecule, and is often in the opposite direction of electroosmotic flow. Both electrophoresis and electroosmosis are often referred to as *electrokinetic* effects, and are of interest in, for example, lab-on-a-chip devices, as reagents can be moved around from place to place on a chip without any moving parts.

If the width of the channel or pore through which fluid is driven is large compared

Figure 1.2: A conceptual illustration of electroosmotic flow. The application of an electric field parallel to the double layer will force the ions in the double layer to move. The rest of the fluid will follow due to the viscous transfer of momentum. The resulting velocity profile will be flat everywhere except in the double layer, where viscous drag from the wall will force the velocity to approach zero.

Figure 1.3: A conceptual illustration of pressure-driven flow. The application of a pressure gradient parallel to the wall will result in a parabolic velocity profile in the channel.

to the width of the double layer region, the velocity in the channel is, for all practical purposes, independent of the channel width and constant across the channel. Fluid flow driven by a pressure gradient, on the other hand, has a velocity that is proportional to the square of the channel width, and has a parabolic velocity profile (see Figure 1.3). This velocity profile can potentially disperse a substance as it is transported down the channel, which can have deleterious effects on operations such

as detection or separation of an analyte. Electroosmosis offers the advantage of a flat velocity profile, which will cause very little dispersion.

1.1.1 Electroosmotic Flow in Porous Media

This work will investigate the modelling of electroosmotic flow in porous materials. Porous materials can be advantageous in lab-on-a-chip devices for a number of different reasons. A relatively small electric field can be used to generate significant pressures, as high pressures are required to force the fluid through very small pores. This implies that electroosmosis can be used to generate high pressures to force fluid through areas that are not exposed to electric fields, and that significant back pressures would be required to prevent flow. Porous materials also offer the capability of filtering analytes based upon their size by the selection of an appropriate pore size, and offer a larger surface area for chemical reactions. Porous segments in a microfluidic device can be used to create regions of high fluidic resistance, while open segments can be used to effectively short two porous regions together. Porous membranes placed between open segments can be used, for example, to separate different analytes based upon their size and diffusion coefficients [5].

The study of electroosmosis in porous materials to date has been devoted primarily to the homogenization of models at the pore scale to develop models at the scale of the porous medium itself. The models typically predict the average volume flow that will result due to an applied voltage gradient. The standard model for electroosmotic flow in porous media does not take viscous shear stresses into account, and thus devices that involve the use of porous segments bordered by open segments, porosity variations within the material, or walls of different charge, cannot easily be modelled.

In this work, a model is developed that enables modelling of electroosmotic flow and pressure-driven flow in porous media of different geometries. This model is found to be compatible with standard theory, but incorporates viscous shear stresses into the model so as to enable modelling fluid flow in porous and open channels, due to electroosmosis or pressure-driven flow. The model is based upon the generalized porous medium equations devised for pressure-driven flow by Vafai and Tien [6] as well as

Nithiarasu et al [7], and thus reduces to the Navier-Stokes equations in the case of an open channel. A model for dispersion in electroosmotic flow at the pore level is developed based upon Taylor's classic analysis of pressure-driven flow in a tube [8,9]. This model is found to be consistent with another result derived independently in the literature [10]. A simple model to estimate dispersion due to electroosmotic flow in porous materials that consist of a distribution of pore sizes is also developed, based upon stochastic models in groundwater flow [11,12]. These models are then used to investigate the flow profiles that result in channels of different geometries with mismatched zeta potentials. Finally the models are compared with experimental results from the chromatography literature, as well as with experimental results from simple microfluidic devices made from nitrocellulose membranes.

1.2 Motivation and Applications

A theory describing electroosmotic flow in porous media could have many possible applications. Electroosmotic flow is routinely used as a method for investigating the surface properties of colloids in chemistry [13], and its use has been investigated in the remediation of contaminated soil [14]. It has been suggested as a possible means for earthquake detection [15], and it has recently been used to devise an electrokinetic battery, in what has been dubbed one of the first new means of generating electricity in many years [16].

One of the major applications for electrokinetic effects to date has been in the separation and identification of different compounds in chemistry and biology. Segments of DNA tend to be negatively charged, and thus will be subject to electrophoresis effects (see Section 1.1) under the influence of an applied electric field. This has been used with great success in the sequencing of the human genome; segments of different length will have different charges and fluidic resistances, and thus can be separated based upon their sequence length. Electroosmosis is used routinely in capillary electrophoresis and capillary electrochromatography as a method for enhancing the separation of different compounds, based upon their charge, chemical properties, diffusion coefficients, and their size.

The theory developed here is intended primarily for modelling microfluidic devices. Microfluidic devices incorporating porous media also have many possible applications. There is considerable interest in automating and miniaturizing the various stages of DNA and protein analysis required for medical diagnostics and pharmaceutical research. In this post-genomic era, it is hoped that it will eventually become possible to identify, for example, which genes are being expressed in a given cell at a given time. This would enable researchers and physicians to determine which of the gene regulatory networks governing a cell's overall health and stability is malfunctioning. A cheap, portable test device capable of performing the required analysis in only a few minutes would completely revolutionize medicine. A more near-term goal would be to develop devices capable of detecting specific proteins in the air, in the water supply, or in blood samples in only a few minutes, rapidly speeding up the diagnosis of diseases or the detection of pathogens. The demand for such devices after the Walkerton water supply tragedy, the anthrax scare in the United States, the recent mad cow scares, SARS, and the recent appearance of the West Nile virus, is obvious. The development and manufacturing of such devices still face many hurdles, including the integration of the various components onto a single chip, improved sensitivity, reproducibility of results, improved yield, and packaging. Researchers require more flexible models and software tools that will enable them to design more sophisticated devices and investigate the different parameters that limit the overall performance of the device. The goal of this thesis is to develop a flexible model for electroosmotic flow in porous media that will help researchers explore new possibilities for microfluidic devices that incorporate porous materials.

1.2.1 Conceptual Examples of Microfluidic Devices

In order to perform such analyses, it will be necessary to be able to inject controlled amounts of different reagents into a device, at precisely controlled intervals. A recent review of microfluidics for lab-on-a-chip applications in general was given by Stone et al [17], and a review for genetic diagnostics in particular was provided by Mastrangelo et al [18]. A simple configuration often used in devices employing electroosmotic flow in open channels for separation applications is shown in Figure 1.4. Different potentials (ϕ_1 , ϕ_2 , ϕ_3 , and ϕ_4) are applied, as needed, at each arm of the intersection to

Figure 1.4: A conceptual illustration of a T-intersection used for sample injection. The arms of each channel would typically have a width on the order of tens of microns. Different potentials (ϕ_n) are applied, as needed, at each arm of the intersection to direct the fluid. Shown here is a sample, injected from the left arm, that has been placed at the channel intersection, ready for separation.

direct the fluid. The sample would be injected at the left arm, and electroosmotic flow would be used to place a narrow plug of material at the channel intersection. The applied potential would then be changed to direct the sample down the separation channel towards the detection window. The separation would result due to electrophoresis of the different molecules in the sample, with possibly the help of a sieving material (such as a gel), that would employ surface effects to aid with the separation.

Lab-on-a-chip devices will need to have more complex control mechanisms by which the fluid can be controlled. Employing more complicated electrokinetic switches enables different samples to be directed to different areas of the chip for different processing, allowing a single microfluidic design to be used for many different applications. An example of an electrokinetic switch from the literature, devised by Lin et al [1], is shown in Figure 1.5. For this configuration, six different potentials are used to direct the fluid from the bottom inlet towards any of the three top channels. The left and right arms are used to help minimize leakage into the other channels.

A microfluidic device designed to perform a typical analysis of DNA will require,

Figure 1.5: A conceptual illustration of an electrokinetic switch, devised by Lin et al [1]. Different potentials (ϕ_n) are applied, as needed, at each arm of the intersection to direct the fluid towards any of the top three channels. The left and right (focus) arms can be used to minimize the leakage into the other channels.

Figure 1.6: A conceptual illustration of a microfabricated device intended for the analysis of genetic material contained in a small population of cells. The cells, injected from the left, are first broken apart using the lysing buffer, followed by the attachment of fluorescent labels to targeted molecules in the cells. These molecules are then attached to probes over the detection window, the probes rinsed, and an array of photodiodes could then be used to detect the fluorescent signal.

for example, the steps of sample injection, amplification, separation or isolation, and detection. These steps may include thermal cycling, mixing with other reagents, or hybridization to any of a wide variety of different probes. Fluorescent labels are often used to facilitate detection, and thus the analysis will often include immobilization

of the DNA probes at designated locations on the chip. A wide variety of different sensors (fiber optic probes, integrated photodiodes, cantilever beams) have been implemented, and a wide variety of different probes are possible (quantum dots, complementary strands of DNA or RNA, antibodies). All of these steps will require the precise control of the fluid used to deliver the analytes to each region of the device, as the concentration profile of the analyte and the timing of its arrival will be critical in any successful analysis. A conceptual diagram illustrating some of the different stages required in such an analysis is shown in Figure 1.6. The sample containing a few of the cells in question (for example, cells from a tumor) are injected from the left. Lysing buffer is then added to break the cells apart, and fluorescent labels attached to the desired segments of DNA or RNA. These segments would then attach to probes bound to the surface of the microfabricated device, causing the fluorescent tags to fluoresce. A rinse step would remove unbound labels from the detection window. Photodiodes could then detect the fluorescent light emitted from the probes. Such an analysis would enable researchers to investigate, for example, the combination of genes that were activated in the cells, helping them discover which genes in the gene regulatory network might be malfunctioning. A recent example of a lab-on-a-chip device capable of cell isolation, lysis, DNA purification and recovery, without any pre- or postsample treatment, was described by Hong et al [19].

1.2.2 Dispersion effects

As mentioned earlier, the timing of the arrival of the different reagents at their desired locations in the device will often be of paramount importance. Unfortunately, an initially flat band of material can become dispersed, or spread out, along the channel as it travels due to the velocity profile in the channel. Slower fluid travelling near the walls will fall behind faster moving fluid travelling in the center of the channel. This process can either be enhanced or retarded by the effects of diffusion. A conceptual illustration of the dispersion process is shown in Figure 1.7. The increase in width of the band of material seen in Figure 1.7(a) could, for example, reduce the strength of a fluorescence signal received from a photodetector, or limit the effectiveness of a desired chemical reaction. For this reason, models taking into consideration the dispersion of an analyte will be important for microfluidic devices. The amount of

Figure 1.7: A conceptual illustration of the dispersion process. (a) An initially narrow band of material at time t_1 will spread out due to the dispersion caused, for example, by the velocity profile in the channel (shown at time t_2). (b) The amount of dispersion seen by an analyte will depend on how quickly molecules in slow moving fluid can diffuse across streamlines to reach faster moving fluid (and vice versa). If the fluid velocity is slow and/or the channel size is small, diffusion will occur fast enough to smooth out changes in the concentration profile induced by the velocity profile. However, if the fluid velocity is fast, and/or the channel size is large, the diffusion across streamlines cannot occur quickly enough, and significant dispersion can result. In general, the dispersion induced by electroosmotic flow is less than that induced by pressure-driven flow.

dispersion caused by the velocity profile in the channel will depend on the channel width, the flow velocity, and the diffusion coefficient. If the fluid velocity is slow and/or the channel size is small, diffusion will occur fast enough to smooth out changes in the concentration profile induced by the velocity profile. This will happen because molecules in the slow-moving fluid near the walls will diffuse into the fast-moving fluid at the channel center, and vice-versa. However, if the fluid velocity is fast, and/or

the channel size is large, diffusion across streamlines cannot occur quickly enough, and significant dispersion can result. Once again, the dispersion due to the velocity profile in electroosmotic flow will, in general, be less than that of pressure-driven flow, because of the flat velocity profile in electroosmotic flow. Dispersion effects in porous media will be more complicated than in open channels, but, in general, they can be minimized if the pore size and fluid velocity are small.

1.2.3 Porous Materials in Microfluidic Devices

As discussed earlier, the use of porous materials in microfluidic devices offers a number of advantages. One of the most important applications for electroosmotic flow in porous materials is in porous electroosmotic pumps [20]. Porous electroosmotic pumps can be used to pump fluid through regions where an electric field is not applied. This can be useful in situations where the use of electric fields must be avoided, for example, to prevent unwanted electrophoresis of the analytes, to help maintain precise temperature control, or to prevent unwanted electrochemical effects from occurring. It is not usually possible to pump fluid using electroosmosis in open channels, because the backpressure of the load regions (the regions outside the electrodes) can be high enough to prevent any net flow at all (see Figure 1.8(c)). In electroosmotic flow, the velocity is independent of the channel width, provided the double layer thickness is thin relative to the width of the channel. For pressure-driven flow, however, the velocity is proportional to the square of the channel width. For this reason, the backpressure of the load regions can become quite large if the channel width is large. However, if electroosmosis is used in a porous region to force the fluid through an open channel, the backpressure of the load will be negligible, because of the small radius of the pores in the porous region. This is illustrated in Figure 1.8(d).

A conceptual illustration of a microfluidic device employing porous electroosmotic pumps is shown in Figure 1.9(a). Using this configuration, it can be seen that fluid can flow in the open channel without exposure to electric fields. The high fluidic resistance of the porous material blocking Inlet 2 would also minimize fluid leakage into the vertical channel. The high fluidic resistance has also been used in Figure

Figure 1.8: Flow profiles due to backpressure effects in open and porous electroosmotic pumps. (a, c) If electroosmosis is used in an open channel to pump fluid through another of equal length, the backpressure of the load can significantly reduce the flow rate. The radius of both the pump and load is $25\ \mu\text{m}$. (b, d) If electroosmosis is used instead in a porous channel to pump fluid through an open channel of equal length, the backpressure of the load will have a very small (often negligible) effect on the flow rate. The radius of both the porous pump and load is $25\ \mu\text{m}$. The flow profile is shown inside a single pore inside the pump, with a radius of approximately $225\ \text{nm}$. The flow profiles have been generated using the theory from Sections 2.2.2 and 4.1.

1.9(b), where two open channels are connected by a porous region. Without the application of an electric field, very little fluid will flow through the center channel, due to its high fluidic resistance. The application of an electric field would connect the two channels, however, allowing the fluid to be directed towards the desired channel.

Porous channels can also be used to help separate different analytes based upon their size, diffusion coefficient, or chemical properties. An illustration of a device capable

Figure 1.9: A conceptual illustration of two different microfabricated devices employing porous materials. (a) A device employing porous electroosmotic pumps to pump fluid through regions outside the electric field. With this configuration, an electric field does not have to be applied along the open channel. Because of the porous material blocking inlet 2, very little fluid will leak into the vertical channel at the intersection. (b) A device employing a porous region with high fluidic resistance to connect two open channels. Without the application of an electric field, very little fluid will flow through the center channel. The application of an electric field would connect the two channels, and fluid would be diverted towards the desired channel.

Figure 1.10: Illustration of a device capable of separating analytes based upon their diffusion coefficients. The analytes to be separated would be injected in the top channel, and diffuse across a porous membrane into a separate stream in the bottom channel [5].

of separating analytes based upon their diffusion coefficients is shown in Figure 1.10. The analytes to be separated would be injected in the top channel, and would then diffuse across a porous membrane into a separate stream in the bottom channel [5]. Molecules with larger diffusion coefficients would diffuse across the membrane faster than molecules with smaller diffusion coefficients. The thickness and porosity of the membrane will affect the separation capabilities of the device.

Perhaps the most successful analytical technique that employs electroosmosis in porous

Figure 1.11: Illustration of a typical capillary electrochromatography (CEC) column. One end of the column is usually packed with porous particles, which are held inside the column using retaining frits. The packed segment is usually followed by an open segment. Electroosmotic flow in the packed segment carries the analytes of interest to the detection window in the open segment. The separating properties of the medium will often be largely due to the surface chemistry of the particles.

media is capillary electrochromatography (CEC) [21, 22]. In CEC, a cylindrical column, typically with a radius on the order of $100\ \mu\text{m}$, is packed with spheres of a few μm in diameter (see Figure 1.11). The cylinder is then filled with a buffer solution that will control the charge on the spheres, and electroosmosis is used to carry a sample towards a detection window. The chromatographic capabilities of the column are due in part from the electrophoresis of the different analytes, but the packing material is responsible for much of the separation resolution of the technique. The surface properties of the material can be altered using different buffer solutions so that specific analytes will be attracted to the surface, slowing them down relative to other analytes that are not attracted to the surface.

In this thesis, a model will be developed that permits the modelling of the devices considered in this section (employing both porous and open channels). This theory will be compared with experimental data from the capillary electrochromatography literature in Chapter 5.

1.3 Thesis Objectives and Contributions

The objective of this work is to develop a general framework for modelling microfluidic devices that incorporate porous media, with a particular focus on the description of electroosmotic flow. To this end, a model based upon the generalized porous medium equations used for pressure-driven flow will be derived, allowing viscous effects near

boundaries and nonlinear momentum effects at higher velocities to be taken into consideration. The formulation used reduces to the Navier-Stokes equations for fluid flow in an open channel when the porosity (or void volume fraction) of the material and the tortuosity (the degree of winding of the pores in the material) approach unity. This makes it possible to model structures incorporating adjacent open and porous channels, porosity variations near a solid boundary, or differences in the zeta potential on the channel walls. This model, although derived independently, can be seen as an extension of Rathore and Horvath's model [23] for electroosmotic flow, which added a viscous term to the standard model for electroosmotic flow in porous media. The model used here reduces to the standard models for electroosmotic flow in cases where the flow velocity is not too high, or viscous effects near the boundaries are negligible. This represents the first flexible model for electroosmotic and pressure-driven flow in porous media intended for microfluidic applications.

Furthermore, models for dispersion in porous media for pressure-driven flow will be applied to electroosmotic flow to help investigate the nature and extent of the dispersion seen by an analyte flowing in a porous medium due to electroosmotic flow. The Taylor dispersion coefficient for electroosmotic flow in a small capillary is calculated, and found to match a result derived independently using a different technique by Griffiths and Nilson [10]. A model for dispersion in heterogeneous porous media for pressure-driven flow is adapted to electroosmotic flow, providing estimates of the growth of the dispersion coefficient over time. This represents the first known model for dispersion in electroosmotic flow in heterogeneous media.

The model is then used to provide analytical results in a number of different geometries, using a one-dimensional model that ignores the viscous effects near the boundaries. Analytical solutions are then provided for a few common geometries with viscous effects near the boundaries taken into consideration. Models are then developed that take into consideration the impact of an increase in porosity and/or potential that occur near the wall in capillaries packed with spheres in capillary electrophoresis. This is the first known model to take both effects into account, and it is shown that the combination of both effects significantly impacts the total volume flow and the dispersion of the analyte.

These models are then used to match the experimental data in the literature for flow in capillary electrochromatography columns. First, the theory is used to predict the average flow speed through a column packed with solid spheres. Then, the flow through a column packed with porous spheres is considered. The model predicts that, although the flow velocities inside the spheres can reach a substantial fraction of the flow velocity between the spheres, only a very small fraction of the volume flow passes through the spheres. The theoretical model is found to provide a good fit to the experimental data. Next, the theory is used to match concentration profiles from the capillary electrochromatography literature. It is found that the theory can be used to match the data, although there is evidence of effects not considered by the model, such as tortuosity variations near the column wall, a time-dependent dispersion coefficient, and thermal gradients in the column.

Finally, experiments using porous nitrocellulose membranes filled with dye are conducted, and the theory is used to predict the dye behaviour over time. The results indicate that the theory is capable of qualitatively matching the general evolution of the dye, but highlights, as well, some of the difficulties encountered in devices incorporating porous media in practice. These results represent the first known attempt to reproduce experimental concentration profiles in electroosmotic flow in porous media.

1.4 Organization

This thesis is organized as follows. In Chapter 2, the background theory for pressure-driven flow in porous media is introduced, followed by the theory for electroosmotic flow in a single pore and some of the existing results for electroosmotic flow in porous media.

In Chapter 3, the model for electroosmotic flow in porous media using the generalized porous medium equation is derived, and a dimensional analysis is used to determine the relative importance of the extra terms. The models for dispersion in electroosmotic flow in porous media are described in Section 3.3.

In Chapter 4, analytical solutions to the proposed model are given for one-dimensional Darcy flows. This is followed by solutions to the Brinkman equation in channels of different geometries, with or without charged walls.

In Chapter 5, the theory is compared with experimental data from the literature, as well as some experiments performed using nitrocellulose membranes.

Finally in Chapter 6, the theory is reviewed, and limitations are discussed, and possible modifications to the theory are considered.

Chapter 2

Literature Review

2.1 Pressure Driven Flow in Porous Media

2.1.1 Describing the geometry of the medium

A porous medium can be modelled as a solid medium filled with hollow, tortuous (winding) capillaries. It can be described geometrically in terms of its void volume fraction, or porosity, ϵ , its pore winding factor, or tortuosity, τ , and its average pore size, a .

For an array of N cylindrical pores, the porosity can be expressed as

$$\epsilon = \frac{V_{void}}{V_{total}} = \frac{N\pi a^2 l}{AL}, \quad (2.1)$$

where l is the length of the cylinder, A is the cross-sectional area of the porous medium, and L is the length of the porous medium. Defining the tortuosity (see Figure 2.1) to be [24]

$$\tau = \left(\frac{l}{L}\right)^2 \quad (2.2)$$

the equation for porosity becomes

$$\epsilon = \frac{N\pi a^2 \sqrt{\tau}}{A}. \quad (2.3)$$

Figure 2.1: Illustration of the tortuosity of a pore. The actual length of the pore is l , while the apparent length of the medium is L .

The effective area, A_e , of the porous medium in this case becomes

$$A_e = N\pi a^2 = \frac{\epsilon}{\sqrt{\tau}} A. \quad (2.4)$$

Typically, the porosity of a material is a measured parameter. It is often measured by comparing the mass of a volume of porous material before water is added to the mass of the same volume after water has been added [24]. In equation form, the porosity can be determined by

$$\epsilon = \frac{m_{wet} - m_{dry}}{\rho_w AL}, \quad (2.5)$$

where m is the mass of the material in question, and ρ_w is the density of water. Other techniques include, for instance, estimating the porosity by imaging a cross-section of the material and calculating the fraction of empty space to the fraction of material in the image.

The tortuosity is a more difficult parameter to characterize, and is often estimated or extracted from experimental data using a model to fit the data. Some authors define the tortuosity as the ratio of conductivity of the fluid in the porous medium to the conductivity of the fluid in an open medium [2], or the ratio of the diffusion constant in the fluid in an open medium to the diffusion constant in the porous medium [3]. The conductivity model can become more complicated if the porous material itself is conductive.

In the following sections, a model will be developed that is based upon the volume-averaged scaling of the Navier-Stokes equations. The volume averaged velocity, $\bar{u}$, is the average volume flow per unit area of the porous medium, which is the apparent velocity with which the fluid flows through a cross-section of material to account for the total volume flow, U . This must be contrasted with the intrinsic average velocity

of the fluid, u_{ave} , which is the actual average velocity at which the fluid is moving inside the winding pores that make up only a fraction of the cross-sectional area of the porous medium. The two can be related by

$$u_{ave} = \bar{u} \frac{A}{A_e} = \bar{u} \frac{\sqrt{\tau}}{\epsilon}. \quad (2.6)$$

This distinction will be important when comparing theory with experimental data, as different techniques are often used to estimate the average velocity. The average velocity could be inferred, for example, either by measuring an increase in fluid volume over time, or by monitoring the time required for a dye in the fluid to travel a certain distance. The first example would be an estimate of the average volume flow, $\bar{u}$, while the second would be an estimate of the intrinsic average velocity in the pores, u_{ave} .

2.1.2 Darcy's Law and the Forchheimer and Brinkman Extensions

Fluid flow in porous media has historically been modelled using empirical relations such as Darcy's Law, which defines a linear relationship between fluid flow and an applied pressure gradient [25, 26, 27]:

$$\bar{u} = -\frac{K}{\mu} \nabla P. \quad (2.7)$$

Here $\bar{u}$ is the volume-averaged fluid velocity in m/s, K is the permeability of the medium in m^2 , μ is the coefficient of viscosity of the medium in kg/(ms), and P is the pressure in N/m^2 . The permeability of the medium is an empirical measure of how permeable it is to water, and is proportional to the cross-sectional area of an individual pore multiplied by the porosity of the medium. It can be considered to be a measure of the resistance of the medium to fluid flow due to an applied pressure gradient. Although Darcy's law was originally a totally empirical relation, it has been derived theoretically a number of times in the literature [28, 29, 26].

Darcy's Law does not take into consideration any viscous effects in the fluid, and thus does not give any information on velocity profiles in a given geometry. Thus,

Darcy's Law was extended by the use of the Brinkman equation [30, 31, 27]:

$$\eta \nabla^2 \bar{u} - \frac{\eta_e}{K} \bar{u} = \frac{\nabla P}{\rho_w} \quad (2.8)$$

where η is the kinematic viscosity of the fluid in m^2/s , η_e is the effective viscosity of the fluid in the porous medium (and is often considered to be the same as η), and ρ_w is the density of the fluid. The viscosity coefficient, μ , is related to the kinematic viscosity by $\mu = \rho_w \eta$.

Brinkman's equation, unfortunately, does not have the capability of incorporating inertial effects at higher flow velocities. An attempt to model the inertial effects in porous media was made by Forchheimer. Forchheimer modified Darcy's Law by adding a nonlinear term to account for the matrix drag, or resistance presented by the porous medium [25, 27, 6, 29]:

$$A\bar{u} + B\bar{u}^2 = \frac{\nabla P}{\rho_w}. \quad (2.9)$$

The terms A (in s^{-1}) and B (in m^{-1}) are empirically obtained parameters that determine the weights of the linear and nonlinear drag terms, and are usually related to the permeability. Unfortunately, Forchheimer's equation does not take viscous effects into consideration. However, one of the most popular models of fluid flow in porous media for many years, Ergun's 1953 semi-empirical relations [32], is formulated as a Forchheimer equation. Although the Forchheimer equation is an empirical relation, a recent theoretical analysis of the Navier-Stokes equations in a porous medium by Whitaker [29] resulted in a $\bar{u}^2$ dependence for the resistance of the medium.

A more flexible approach that can account for the effects of viscosity, inertia, and changes in porosity, is to incorporate the porosity and tortuosity of a porous medium directly into the Navier-Stokes equations [6, 7, 33, 27]. This approach is the one that will be used throughout this work, and will be explained in detail in Section 2.1.4.

2.1.3 Permeability Models

The permeability is the most important, and probably the most difficult, parameter of the porous medium to characterize. Today, it still remains largely empirical in nature, as it is, for all practical purposes, impossible to completely characterize the geometry of the medium upon which the permeability depends.

As mentioned earlier, one of the most widely used definitions of permeability is based upon Ergun's 1953 empirical relations [32], which in turn are based loosely upon the Carman-Kozeny definition of permeability [25].

Kozeny modelled fluid flow through a packed bed by assuming the medium was composed of hollow, tortuous capillaries. Fluid flow through a narrow capillary can be modelled using the Navier-Stokes equations, which are given by

$$\frac{\partial u}{\partial t} + u \cdot \nabla u = -\frac{\nabla P}{\rho_w} + \eta \nabla^2 u + g + F \quad (2.10)$$

$$\nabla \cdot u = 0, \quad (2.11)$$

where u denotes the (unscaled) fluid velocity in the capillary. The second term on the left of the first equation is nonlinear, and accounts for the inertia of the fluid. The second term on the right accounts for viscous effects in the fluid. The g term describes the gravitational effects on the fluid. The F term accounts for external forces on the fluid. The second equation is the continuity equation, which ensures the conservation of mass. It will be assumed throughout this work that the fluid is incompressible. If the flow is steady and horizontal, the partial derivative with respect to time and the gravity term can be neglected.

It can be shown [34] that if the radius of the pore and/or the velocity of the fluid is very small, the nonlinear momentum terms can be neglected, and the flow is thus governed by

$$\eta \nabla^2 u = \frac{\nabla P}{\rho_w}. \quad (2.12)$$

For reasons of symmetry, flow in the radial direction can also be neglected. It will be assumed that the pressure gradient is in the axial direction only. In cylindrical coordinates, then, the flow, which is also only in the axial direction, is governed by

$$\frac{1}{r} \frac{d}{dr} \left(r \frac{du}{dr} \right) = \frac{\nabla P}{\mu}. \quad (2.13)$$

The solution to this equation, applying the no-slip condition on the capillary wall ($u = 0$ at $r = a$), is

$$u = \frac{\nabla P}{\mu} \left(\frac{a^2 - r^2}{4} \right). \quad (2.14)$$

This well-known solution is often called Poiseuille flow, and is known for its parabolic velocity profile. The average volume flow, U_{ave} , can be found by integrating over the cross-sectional area of the capillary and dividing by the area, and is given by

$$U_{ave} = \frac{a^2}{8} \frac{\nabla P}{\mu}. \quad (2.15)$$

In porous media, flow can be modelled as flowing through a large number of tortuous capillaries of different shapes. Poiseuille's law for volume flow can be generalized to channels of different geometries as [25]

$$U_{ave} = \frac{m^2}{k_o} \frac{\nabla P}{\mu}, \quad (2.16)$$

where m is the mean hydraulic radius, defined as

$$m = \frac{\text{cross-sectional area normal to flow}}{\text{perimeter presented to fluid}}. \quad (2.17)$$

The k_o term is a shape factor that changes for channels of different geometries. For a cylinder, $m = \frac{a}{2}$, and $k_o = 2$. For channels of other geometries, k_o can range from 0.812 to 3 [33, 25]. It turns out that many different types of channels have k_o values of approximately 2, which may explain why models of porous media using arrays of cylinders have been so successful [25].

If the cross-section of the pipe is assumed to be uniform, the mean hydraulic radius, m , can also be defined as

$$m = \frac{\text{volume of fluid in pipe}}{\text{surface presented to fluid}}. \quad (2.18)$$

In a porous medium composed of hollow, tortuous capillaries, m can instead be defined by

$$m = \frac{\text{volume of fluid in medium}}{\text{surface presented to fluid}}. \quad (2.19)$$

Dividing both the numerator and denominator by the total volume of the porous medium, m can then be expressed in terms of the medium's porosity, ϵ , as

$$m = \frac{\epsilon}{S} \quad (2.20)$$

where S is the surface area per unit volume of the solid matrix.

In a porous medium, the fluid will be able to flow through only a portion of the cross-sectional area, and thus scaling arguments must be used to account for the medium's porosity and tortuosity when determining its average volume flow. Letting uA_e be the volume flow with velocity u through an effective cross-sectional area A_e , and defining $\bar{u}$ as the effective velocity of a fluid through the actual cross-sectional A , assigning the volume flow to be equal in both cases results in the relationship

$$uA_e = \bar{u}A \quad (2.21)$$

which can be rearranged to give

$$\bar{u} = \frac{uA_e}{A} = \frac{\epsilon}{\sqrt{\tau}}u. \quad (2.22)$$

Letting X be a length scale in the porous medium at the macroscopic scale, and x be a length scale in the porous medium at the pore level, the two length scales can then be related by

$$\frac{x}{X} = \frac{l}{L} = \sqrt{\tau}, \quad (2.23)$$

where equation 2.2 has been used. Thus, all spatial derivatives will be scaled by the square root of the tortuosity using

$$dx = \sqrt{\tau} dX. \quad (2.24)$$

Using the scaling arguments in equations 2.22 and 2.24, one obtains Carman's version of Kozeny's equation for flow in porous media [25]:

$$\bar{u} = \frac{\epsilon m^2}{\sqrt{\tau} k_o} \frac{\nabla P}{\sqrt{\tau} \mu}, \quad (2.25)$$

where $\bar{u}$ denotes the volume-averaged velocity in the porous medium. According to Darcy's Law, then, the permeability is given by

$$K = \frac{\epsilon m^2}{\tau k_o}. \quad (2.26)$$

Inserting equation 2.20 into equation 2.25, one obtains

$$\bar{u} = \frac{\epsilon^3}{\sqrt{\tau} S^2 k_o} \frac{\nabla P}{\sqrt{\tau} \mu}. \quad (2.27)$$

In some cases, it is more convenient to model the porous medium as being composed of many solid spheres rather than hollow capillaries. For a bed of spheres, the surface area per unit volume, S , in terms of the solid particle diameter, d_p , is

$$S = \frac{N\pi d_p^2}{AL}, \quad (2.28)$$

while the porosity is

$$\epsilon = \frac{AL - N\frac{\pi d_p^3}{6}}{AL}. \quad (2.29)$$

Inserting this definition of porosity in the equation for S one obtains

$$S = \frac{6(1 - \epsilon)}{d_p}. \quad (2.30)$$

Inserting these equations into equation (2.25), the Kozeny-Carman equation yields

$$\bar{u} = \frac{\epsilon^3 d_p^2}{36\sqrt{\tau}k_o(1-\epsilon)^2} \frac{\nabla P}{\sqrt{\tau}\mu}. \quad (2.31)$$

The Kozeny-Carman permeability can thus be expressed as

$$K = \frac{\epsilon^3 d_p^2}{36\tau k_o(1-\epsilon)^2}. \quad (2.32)$$

The $\frac{\epsilon^3}{(1-\epsilon)^2}$ dependence on the porosity has been found to correlate very well with experimental data in spherical beds [25, 32] at low flow rates (i.e. at low Reynolds number). Ergun [32] found that much of the data correlated very well for both low and higher flow rates with a Forchheimer-like expression given by

$$\frac{\Delta P}{L} = 150 \frac{(1-\epsilon)^2}{\epsilon^3 d_p^2} \mu \bar{u} + 1.75 \frac{(1-\epsilon)}{\epsilon^3} \frac{\rho_w \bar{u}^2}{d_p}, \quad (2.33)$$

which can be expressed in terms of the permeability as

$$\frac{\Delta P}{L} = \frac{\mu \bar{u}}{K} + \frac{1.75 \rho_w \bar{u}^2}{\sqrt{150K} \epsilon^3} \quad (2.34)$$

provided that the permeability is defined as

$$K = \frac{\epsilon^3 d_p^2}{150(1-\epsilon)^2}. \quad (2.35)$$

This implies that $36k_o\tau = 150$, or $k_o\tau \approx 4.17$. If k_o is assumed to be 2 (that of a cylinder), this implies that $\tau \approx 2$, a value that is often found in the literature. Ergun's relations are some of the most frequently used expressions for permeability in the literature. They are often used to fit a more general Forchheimer expression of the form [27]

$$F = \frac{\mu \bar{u}}{K} + \frac{F_\epsilon \rho_w \bar{u} |\bar{u}|}{\sqrt{K}} \quad (2.36)$$

where F_ϵ is given (using the Carman-Kozeny model for the permeability combined with Ergun's relations) as

$$F_\epsilon = \frac{1.75}{\sqrt{36\epsilon^3 k_o \tau}}. \quad (2.37)$$

The absolute value in the $\bar{u}|\bar{u}|$ term is necessary in order to preserve the direction of the velocity.

Another definition for the permeability often encountered in the literature is that of Burke and Plummer [32, 25], which involves the use of Stokes' drag on a bed of spheres. This results in a definition of permeability at low flow rates that is off by a factor of $\frac{\epsilon}{(1-\epsilon)}$, which is not supported by the experimental data at low flow rates. However, at higher flow rates, Burke and Plummer's theory shows the kinetic energy loss to be proportional to $\frac{(1-\epsilon)}{\epsilon^3}$, which can be seen to match the quadratic velocity term in Ergun's relations (2.33). The reasons for the inadequacy of this model have yet to be satisfactorily explained. Because the definition based upon Stokes' drag is not supported by the experimental data at lower flow rates, it will not be used in this work.

For media composed of different materials, an effective solid particle diameter is usually used. A commonly used definition for the effective solid particle diameter is [26]

$$d_p = 6 \frac{V_s}{A_s}, \quad (2.38)$$

where V_s and A_s are the volume and surface area of the solid phase. For a medium composed of hollow tortuous cylinders, this can be expressed as

$$d_p = 6 \frac{AL - N\pi a^2 l}{N2\pi a l} = 6 \frac{1 - \frac{N\pi a^2 l}{AL}}{\frac{N2\pi a l}{AL}} = 6 \frac{1 - \epsilon}{\epsilon(2/a)} = \frac{3a(1 - \epsilon)}{\epsilon}, \quad (2.39)$$

where equation 2.1 for the porosity has been used. The Kozeny-Carman permeability for a medium of hollow cylinders can thus be expressed as

$$K = \frac{\epsilon a^2}{4\tau k_o}. \quad (2.40)$$

Inserting this into Darcy's law (equation 2.7), with $k_o = 2$, results in

$$\bar{u} = \frac{\epsilon a^2}{8\tau} \frac{\nabla P}{\mu}, \quad (2.41)$$

which is simply the Poiseuille average flow velocity scaled by the effective area and the square root of the tortuosity. This simple scaling is often found in the literature, such as, for example, in Zeng's [24] model for electroosmotic flow in porous media.

The definition for the permeability that will be used throughout this work will be cast in a slightly different form than that in equations 2.36 and 2.37. The formulation that will be used instead (see Section 2.1.4) accounts for the $\sqrt{\tau}$ scaling due to the applied pressure or voltage gradient elsewhere. Therefore, the Kozeny-Carman permeability used in this work will be expressed as

$$K = \frac{\epsilon^3 d_p^2}{36 k_o \sqrt{\tau} (1 - \epsilon)^2}, \quad (2.42)$$

and F_ϵ will be given instead by

$$F_\epsilon = \frac{1.75}{\sqrt{36 \epsilon^3 k_o \sqrt{\tau}}}. \quad (2.43)$$

In order to switch back and forth between models that are defined in terms of the solid particle diameter of the medium, d_p and the average pore size, a , equation 2.39 will be used frequently. This permits the use of equation 2.40, which will be recast in the form

$$K = \frac{\epsilon a^2}{4 \sqrt{\tau} k_o}. \quad (2.44)$$

Finally, it must be noted that the permeability of a real porous medium will often be an anisotropic quantity, and thus must be represented as a tensor. Due to the complicated nature of real porous media, flow models will usually need to be fine-tuned to fit the material in question.

2.1.4 The Generalized Porous Medium Equation

Flow in porous media can be modelled with more flexibility using a generalized porous medium equation, in which the Navier-Stokes equations are scaled to model the average volume flow through the porous medium [6, 27, 7]. Once again, the incompressible Navier-Stokes equations are given by

$$\frac{\partial u}{\partial t} + u \cdot \nabla u = -\frac{\nabla P}{\rho_w} + \eta \nabla^2 u + g + F, \quad (2.45)$$

plus the continuity equation 2.11.

As shown previously, the velocity terms must be scaled by the effective area, as shown originally in equation 2.22:

$$\bar{u} = \frac{u A_e}{A} = \frac{\epsilon}{\sqrt{\tau}} u. \quad (2.46)$$

Similarly, all spatial gradients must be scaled by the square root of the tortuosity, as in equation 2.24:

$$dx = \sqrt{\tau} dX. \quad (2.47)$$

Expressing the Navier-Stokes equations in terms of the effective velocity $\bar{u}$ and the macroscopic length scale X , one obtains

$$\frac{\sqrt{\tau}}{\epsilon} \frac{\partial \bar{u}}{\partial t} + \frac{\sqrt{\tau}}{\epsilon} \bar{u} \cdot \nabla \left(\frac{\bar{u}}{\epsilon} \right) = -\frac{\nabla P}{\sqrt{\tau} \rho_w} + \frac{\eta}{\sqrt{\tau}} \nabla^2 \left(\frac{\bar{u}}{\epsilon} \right) + g + F. \quad (2.48)$$

Finally, in order to model fluid flow in porous media, one has to take into account matrix drag effects, i.e. the drag represented by the solid portion of the medium. This is usually done by adding a Forchheimer force, described in terms of the permeability of the medium, to the Navier-Stokes equations. The Forchheimer force can be expressed using Ergun's relations [32] as

$$F = -\frac{\eta_e \bar{u}}{K} - \frac{F_e \bar{u} |\bar{u}|}{\sqrt{K}} \quad (2.49)$$

where F_ϵ is given by equation 2.43 in the previous section.

This formulation is identical to the model by Vafai and Tien [6] as seen in the book by Nield and Bejan [27], as well as the model by Nithiarasu et al [7], except that, in this case, the tortuosity has been used as well in the scaling. Although Nithiarasu used fairly similar scaling arguments, more sophisticated volume averaging techniques were used by Vafai and Tien, as well as Liu and Masliyah [33]. Although the tortuosity was considered by Liu and Misliyah, their formulation is slightly different than the one used here. It should be noted that setting both τ and ϵ to one yields the Navier-Stokes equations, which enables modelling of fluid flow in adjacent porous and open channels.

2.1.5 Peclet numbers and Taylor Dispersion

The above macroscopic theory for flow in porous media takes no account of the velocity profiles in an individual pore. However, any solute carried along with the fluid by convection will be dispersed according to the velocity profile in each pore. Dispersion will also occur at the junctions of different pores, or when the fluid is forced to flow around solid obstacles. Dispersion in porous media is a complicated phenomenon that is still very much a topic of research.

Figure 2.2: A conceptual illustration of the dispersion process for pressure-driven flow in a single pore. The amount of dispersion seen by an analyte will depend on how quickly molecules in slow moving fluid can diffuse across streamlines to reach faster moving fluid (and vice versa). If the fluid velocity is slow and/or the channel size is small, diffusion will occur fast enough to smooth out changes in the concentration profile induced by the velocity profile. However, if the fluid velocity is fast, and/or the channel size is large, the diffusion across streamlines cannot occur quickly enough, and significant dispersion can result.

The degree of dispersion that occurs due to the fluid motion depends largely on the velocity of the fluid, the characteristic dimension of the fluid medium, and the

diffusion constant (in m^2/s). For systems in which the fluid flow is very fast and/or the channel radius is very large, diffusion of the solute will not be sufficient to smooth any changes in concentration profile introduced by the fluid motion (see Figure 2.2). However, for systems in which the flow speed is very slow and/or the channel radius is small, the solute can diffuse across the channel quite quickly and eliminate the concentration gradients induced by fluid motion. This tradeoff can be expressed quantitatively using a non-dimensional number known as the Peclet number, P_e , which, for channels of radius a can be defined as the ratio

$$P_e = \frac{u_{ave}a}{D} \quad (2.50)$$

where u_{ave} is the average velocity in the channel and D is the diffusion coefficient. A small Peclet number implies that diffusion effects are dominant, while a larger Peclet number implies that the velocity effects dominate. Thus, studies of dispersion, such as those by Koch and Brady [35] or Liu et al [33] typically analyze its dependence on P_e .

Initially, only the dispersion due to the velocity profile in a single pore will be considered. It was shown by Taylor [8] for flow in a cylinder and, more generally, by Aris [9], that the amount of dispersion can be represented in terms of an effective diffusion coefficient. The process of dispersion due to the fluid velocity profile is thus often called Taylor or Taylor-Aris dispersion.

For tubes of circular cross-section, Taylor was able to show that the effective diffusion constant is given by

$$D_{eff} = D + \frac{u_{ave}^2 a^2}{48D} = D \left(1 + \frac{P_e^2}{48} \right). \quad (2.51)$$

The factor of 48 in the denominator on the right is a result of the Poiseuille (parabolic) velocity profile due to pressure-driven flow in a cylinder. As expected, diffusion effects dominate at small Peclet numbers, and the effective diffusion constant only becomes noticeably larger than the actual diffusion constant for larger Peclet numbers. Fluid flow at 1 mm/s, in a pore of 500nm radius, with a diffusion constant of 5×10^{-9}

m^2/s , will have a Peclet number of 0.1, and will have an effective diffusion coefficient of 5.001×10^{-9} , i.e. the dispersion is negligible. Fluid flow at 10 mm/s in a pore of $5\mu m$ radius, however, will have a Peclet number of 10, and an effective diffusion coefficient of $2.08 D$, and thus dispersion must be considered.

Thus, velocity profiles at the pore level can be incorporated into a macroscale model through the use of an effective diffusion coefficient. This coefficient would apply in the direction of fluid flow, and thus would cause the overall diffusion coefficient to become anisotropic.

2.2 Electroosmosis

2.2.1 Double Layer Theory

When a charged surface is in contact with a solution, electroneutrality requires that ions of the opposite sign in the solution accumulate near the surface in order to neutralize the surface charge. The density of the ions is highest close to the surface, and decays rapidly (typically exponentially) away from the charged surface. This diffuse region of charge is typically called, for historical reasons, the *double layer* [36, 13]. The thickness of the layer depends on the concentration and charge magnitude of the ions in the solution. Higher concentration solutions have more ions with which to neutralize the surface charge, and thus thinner double layers result.

Due to the finite size of the ions, there is, in fact, a third region between the surface and the double layer. This region is only a few angstroms in thickness, and is charge free. The thickness of this region depends largely on the extent to which the ions remain hydrated near the surface. This *inner* or *compact* region is often referred to as the *Stern* or *Helmholtz* layer. The picture can be further complicated if ions in the solution can be adsorbed onto the surface. The pH of a given solution will typically have a major impact on the surface potential due to adsorption. These concepts are illustrated in Figure 2.3.

Figure 2.3: Illustration of the anatomy of the double layer. Ions of opposite charge in the fluid will be attracted to the charged surface, forming a double layer that shields the rest of the channel from the wall potential. The charge density of ions will approach zero quickly away from the wall.

The electrokinetic properties of colloidal systems are controlled largely by the potential that occurs at the interface between the Stern layer and the diffuse double layer [36, 13]. Measurement of the potential at this interface is usually not possible, so instead, the potential at the *surface of shear* or *slipping plane*, is usually used. The region inside the Stern layer is usually considered to be held immobile due to electrostatic forces, as well as the first few layers of solvent. The interface where the solvent is free to move is defined as the surface of shear. The potential at this interface is called the *zeta potential*, denoted in this work as ψ_o . It is usually used as an approximation of the potential at the interface between the Stern layer and the diffuse double layer. In this work, it will be assumed that the potential at the surface is equal to the zeta potential.

The charge density in the double layer decays rapidly as one moves away from the surface of shear. The thickness of the double layer is typically described in terms of its *Debye length*, which is approximately the distance required for the charge density to reach e^{-1} (36.7%) of its value at the surface of shear.

If an electric field is applied parallel to the charged surface, ions in the diffuse double layer will move in response, and the fluid will follow due to viscous drag (see Figure

Figure 2.4: A conceptual illustration of electroosmotic flow. The application of an electric field parallel to the double layer will force the ions in the double layer to move. The rest of the fluid will follow due to the viscous transfer of momentum. The resulting velocity profile will be flat everywhere except in the double layer, where viscous drag from the wall will force the velocity to approach zero.

2.4). The velocity of the fluid remains constant at its maximum value outside the double layer, and varies within the double layer according to the potential distribution in that region, reaching zero at the surface of shear. This particular electrokinetic effect is called *electroosmosis*.

A related electrokinetic effect occurs, if, instead, a pressure gradient is applied. The fluid will again be forced to move, causing ions in the double layer to move with the flow. This current causes charge to accumulate downstream, permitting a potential difference to be set up against the pressure gradient. This potential is called the *streaming potential*.

These concepts can be described mathematically for a small pore with charged walls as follows. The potential distribution in the double layer, ψ , can be determined by Poisson's equation,

$$\nabla^2 \psi = -\frac{\rho}{\epsilon_w}, \quad (2.52)$$

where ρ is the charge density in the pore and ϵ_w is the permittivity of the fluid. The charge density is found from the Boltzmann equation [36, 13], which, for N species is

given by

$$\rho = e \sum_i^N n_i^o z_i, \quad (2.53)$$

where z_i is the charge on the i th species, e is the charge of an electron, and n_i^o , the concentration of the i th species with bulk concentration n_i , is given by

$$n_i^o = n_i e^{-\frac{e z_i \psi}{kT}}, \quad (2.54)$$

where k is Boltzmann's constant. Boltzmann's equation accounts for the fact that negative ions will be concentrated in regions of positive potential, whereas positive ions will be repelled, and vice-versa for regions of negative potential [36, p. 128].

By combining Boltzmann's equation with the Poisson equation, the Poisson-Boltzmann equation is obtained:

$$\nabla^2 \psi = -\frac{e \sum_i^N n_i z_i e^{-\frac{e z_i \psi}{kT}}}{\epsilon_w}. \quad (2.55)$$

For simplicity, a binary, univalent solution (such as NaCl, for example), will be considered, so that Boltzmann's equation for the charge density can be expressed as

$$\rho = -2n^o z e \sinh\left(\frac{ze\psi}{kT}\right). \quad (2.56)$$

If the zeta potential is not too large, the hyperbolic sine, $\sinh$, term can be linearized so that the charge density is given by

$$\rho = -\frac{2n^o z^2 e^2}{kT} \psi \quad (2.57)$$

and thus the linearized Poisson-Boltzmann equation is given by

$$\nabla^2 \psi = \left(\frac{2n^o z^2 e^2}{\epsilon_w kT}\right) \psi. \quad (2.58)$$

The square root of the term in brackets has units of $1/m$, and is a measure of the thickness of the double layer. It is termed the Debye-Huckel parameter, or inverse

Debye length, and is denoted κ . It is defined by

$$\kappa = \sqrt{\frac{e^2 \sum_i^N n_i^o z_i^2}{\epsilon_w kT}} = \sqrt{\frac{2n^o z^2 e^2}{\epsilon_w kT}} \quad (2.59)$$

for a binary, univalent solution. The linearized Poisson-Boltzmann equation can then be expressed as

$$\nabla^2 \psi = \kappa^2 \psi, \quad (2.60)$$

and the charge density is therefore given by

$$\rho = -\frac{2n^o z^2 e^2}{kT} \psi = -\epsilon_w \kappa^2 \psi. \quad (2.61)$$

Technically, this linearization is valid only when the zeta potential is small, or, more precisely, the ratio $\frac{ze\psi}{kT} \ll 1$. At room temperature, this implies that $\psi \ll 25.4mV$. However, it has been found that this approximation remains valid up to approximately $50mV$ [37, 13]. This is fortunate, because the full analytical solution to the original, nonlinear equation is not usually possible.

In 1-D, the solution to equation 2.60, with a surface of potential $\psi = \psi_o$ located at $x = 0$, is given by

$$\psi = \psi_o e^{-\kappa x}. \quad (2.62)$$

Thus, the potential has a maximum value of ψ_o at the surface, and exponentially decreases as one moves away from the surface. Although the thickness of the double layer is usually referred to in terms of its Debye length as $\frac{1}{\kappa}$, in actual fact it would be better approximated as $\frac{3}{\kappa}$ or $\frac{4}{\kappa}$. As seen in equation 2.59, the thickness of the double layer increases as the solute concentration decreases, and decreases as the concentration increases. A solution with a larger concentration has more ions that can be used to neutralize the wall charge, and, thus, a smaller double layer region develops.

2.2.2 Electroosmotic Flow (EOF) in a Single Pore

Electroosmotic flow occurs when ions in the double layer move under the influence of an applied electric field, causing the fluid to follow due to viscous drag. Here, the Poisson-Boltzmann equation will be coupled with the fluid dynamics to describe electroosmotic flow in a small pore.

Assuming that the fluid is viscous and incompressible, fluid flow in a single pore can be modelled using the Navier-Stokes equations, with an extra force term, ρE , where E is the electric field, to incorporate the electroosmotic force:

$$\frac{\partial u}{\partial t} + u \cdot \nabla u = -\frac{\nabla P}{\rho_w} + \eta \nabla^2 u + g + \frac{\rho E}{\rho_w} \quad (2.63)$$

$$\nabla \cdot u = 0. \quad (2.64)$$

In this analysis, it will be assumed that the flow is steady, and that the effects of gravity can be neglected. Furthermore, it can be shown [34, p.31, p.239] that, if the pore radius and/or the fluid velocity is very small, the non-linear momentum term can also be neglected. Thus, the Navier-Stokes equation reduces to

$$\eta \nabla^2 u = \frac{\nabla P}{\rho_w} - \frac{\rho E}{\rho_w} \quad (2.65)$$

The linear nature of this equation allows it to be broken up into two components, a pressure-driven component, and an electroosmotic flow (EOF) component. The solution to the pressure-driven component has already been given in section 2.1.3. The EOF component can be determined by inserting the Poisson-Boltzmann equation (2.52) into equation 2.65:

$$\nabla^2 u = \frac{\epsilon_w \nabla^2 \psi E}{\mu}. \quad (2.66)$$

It will be assumed that the pore is cylindrical in shape with radius a , and that it is long enough that changes in the axial direction occur on a length scale large enough to be neglected. Due to the symmetric nature of the problem, the radial velocity component can also be neglected. It will also be assumed that the double layer is very thin relative to the distance between electrodes; thus the electric field over the

double layer will be much stronger than the applied electric field parallel to the pore wall, allowing the fields to be decoupled and treated separately.

In cylindrical coordinates with these assumptions, equation 2.66 becomes

$$\frac{1}{r} \frac{d}{dr} \left(r \frac{du}{dr} \right) = \frac{\epsilon_w E}{\mu} \frac{1}{r} \frac{d}{dr} \left(r \frac{d\psi}{dr} \right). \quad (2.67)$$

Multiplying by r and integrating each side results in

$$r \frac{du}{dr} = \frac{\epsilon_w E}{\mu} \left(r \frac{d\psi}{dr} + b \right). \quad (2.68)$$

By symmetry, all gradients at the center of the pore ($r = 0$) must be zero, and thus $b = 0$. Integrating once again with respect to r results in

$$u(r) = \frac{\epsilon_w E}{\mu} \psi(r) + c. \quad (2.69)$$

The constant c can be determined by applying the boundary conditions $u = 0$ and $\psi = \psi_o$ at the pore surface, $r = a$. The velocity profile in the pore is thus given by

$$u(r) = \frac{\epsilon_w \psi_o E}{\mu} \left(\frac{\psi(r)}{\psi_o} - 1 \right). \quad (2.70)$$

At the pore surface, $\psi = \psi_o$, and thus the velocity is zero. Outside the double layer, $\psi \simeq 0$, and the velocity reaches a constant value whose magnitude is determined by the zeta potential, the applied electric field, the viscosity, and the permittivity of the fluid. In many cases of practical interest, the radius of the pore is large relative to the thickness of the double layer, and thus the thin double layer region, in which the velocity goes to zero, can be neglected. The fluid velocity in the pore can thus be assumed to be independent of position in the pore, and be described by

$$u = -\frac{\epsilon_w \psi_o E}{\mu}. \quad (2.71)$$

Equation 2.71 is a general result that is independent of the shape of the pore, and is generally attributed to Von Smoluchowski [36, 13]. The velocity profile in electroosmotic flow is often referred to as plug-like, due to its very flat profile. This flat profile is important as it minimizes the dispersion of an analyte in the fluid.

In cases where the pore radius is not much larger than the thickness of the double layer, the double layer region cannot be neglected, and thus the $\psi(r)$ term in equation 2.70 must be taken into consideration. An analytical expression for the potential distribution can be obtained by solving the linearized Poisson-Boltzmann equation 2.60. This problem was first tackled in cylindrical coordinates by Rice and Whitehead [37], and is given by

$$\frac{1}{r} \frac{d}{dr} \left(r \frac{d\psi}{dr} \right) = \kappa^2 \psi. \quad (2.72)$$

Multiplying by r^2 , expanding the left hand side and rearranging, one obtains

$$r^2 \frac{d^2\psi}{dr^2} + r \frac{d\psi}{dr} - \kappa^2 r^2 \psi, \quad (2.73)$$

which is a modified Bessel equation of order zero. The solution is therefore given by

$$\psi(r) = AI_o(\kappa r) + BK_o(\kappa r), \quad (2.74)$$

where I_o and K_o are zero order modified Bessel functions of the first and second kind, respectively, and A and B are constants. Applying the boundary condition $\psi(a) = \psi_o$ at the pore surface, and noting that B must be zero because K_o is infinite at $r = 0$, the potential in the pore is therefore given by

$$\psi(r) = \psi_o \frac{I_o(\kappa r)}{I_o(\kappa a)}. \quad (2.75)$$

Inserting equation 2.73 into equation 2.70 for the velocity profile, one obtains

$$u(r) = \frac{\epsilon_w \psi_o E}{\mu} \left(\frac{I_o(\kappa r)}{I_o(\kappa a)} - 1 \right). \quad (2.76)$$

Figure 2.5: Charge density profiles in a pore for different κa ratios in the case of low zeta potentials.

Figure 2.6: Velocity profiles in a pore for different κa ratios in the case of low zeta potentials. The velocity profile for pressure driven flow is also shown for comparison.

The linearized charge density and velocity profiles in a single pore are illustrated in

Figures 2.5 and 2.6, respectively. Both the potential and velocity profiles in the pore are governed by the ratio of the Debye length to the pore radius, κa . If the pore radius is only a few times larger than the Debye length, i.e. the κa ratio is less than 10, the double layer region accounts for a large fraction of the total pore cross-sectional area, and, thus, the flow profile is not plug-like (flat). At $\kappa a = 2$, the profile is almost parabolic in nature. However, for larger κa ratios, the flow profile quickly becomes very flat. Typically, double layer effects are only considered if the κa ratio is less than 50. The Debye length for double layers of different solutions typically ranges from less than 1 nm to a few hundred nm, depending on the concentration of the solution in the pore.

The volume flow in the pore can be found by integrating equation 2.76 over the cross-sectional area of the pore. This results in

$$U = \frac{\epsilon_w \psi_o EA}{\mu} \left(\frac{2I_1(\kappa a)}{\kappa a I_o(\kappa a)} - 1 \right), \quad (2.77)$$

where U is the volume flow in the pore, A is the cross-sectional area, and $I_1(\kappa a)$ is a modified Bessel function of the first kind of order one. For large κa ratios, the ratio of Bessel functions goes to zero. The dependence on the κa ratio is plotted in Figure 2.7. Note that this equation can also be expressed in a more compact but less intuitive form as

$$U = -\frac{\epsilon_w \psi_o EA}{\mu} \left(\frac{I_2(\kappa a)}{I_o(\kappa a)} \right), \quad (2.78)$$

where $I_2(\kappa a)$ is a modified Bessel function of the first kind of order two.

The solutions for electroosmotic flow (2.76) and pressure-driven flow (2.14) in a small capillary can be added to determine the velocity profile in a capillary under the influence of both an axial voltage and pressure gradient. The velocity profile is given by

$$u(r) = \frac{\nabla P}{\mu} \left(\frac{a^2 - r^2}{4} \right) + \frac{\epsilon_w \psi_o E}{\mu} \left(\frac{I_o(\kappa r)}{I_o(\kappa a)} - 1 \right). \quad (2.79)$$

Figure 2.7: Volume flow dependence on κa ratios in the case of low zeta potentials.

The solution for volume flow is

$$U = \frac{a^2}{8} \frac{\nabla P A}{\mu} + \frac{\epsilon_w \psi_o E A}{\mu} \left(\frac{2I_1(\kappa a)}{\kappa a I_o(\kappa a)} - 1 \right). \quad (2.80)$$

The counter pressure required to yield a net zero volume flow can be found by setting the left hand side of equation 2.80 to zero. The result is

$$\left(\frac{\nabla P}{E} \right)_{cp} = \frac{8\epsilon_w \psi_o}{a^2} \left(1 - \frac{2I_1(\kappa a)}{\kappa a I_o(\kappa a)} \right). \quad (2.81)$$

It is apparent that the pressure required to stop the flow increases rapidly as the pore radius a decreases. Thus, electroosmotic flow is expected to be more efficient than pressure-driven flow in very small pores. Backpressure buildup is also expected to be less of a problem in devices employing small pores, so long as the κa ratio is large enough that the double layer effects are negligible. This implies that devices employing electroosmosis in porous materials will be relatively insensitive to backpressure effects.

2.2.3 The Streaming Potential

If a pressure gradient is applied across a capillary filled with an electrolyte solution, a convection current will flow due to the movement of charge with the fluid. The accumulation of charge at the ends of the capillary will cause a potential to develop across the capillary so as to prevent a net current flow in either direction. This potential, called the *streaming potential*, is often used to measure the zeta potential of a material.

Following the treatment by Rice and Whitehead [37], the current in the capillary is given by

$$i = i_1 + i_2 = \left(2\pi \int_0^a u(r) \rho(r) r dr \right) + (\sigma_o E A_p + 2\pi a \sigma_s E), \quad (2.82)$$

where i_1 is the convection current, i_2 is the conduction current, σ_o is the conductivity of the fluid, σ_s is the surface conductivity of the wall, and A_p is the cross-sectional area of the pore. The convection current is found by the first bracketed term on the righthand side, while the conduction current is found by the second bracketed term. The streaming potential can be found by determining the potential required to set i to zero. If the zeta potential is small enough that the Poisson-Boltzmann equation can be linearized, the velocity profile, $u(r)$, which contains contributions from both pressure driven and electroosmotic flow, will be given by equation 2.79, and the charge density $\rho(r)$ by equations 2.61 and 2.75. Carrying out the integration in equation 2.82, the total current can be expressed as

$$i = \sigma_o E A_p \left[1 + \frac{2\sigma_s}{a\sigma_o} + \frac{\epsilon_w^2 \kappa^2 \psi_o^2}{\sigma_o \mu} \left(\frac{I_1^2(\kappa a)}{I_o^2(\kappa a)} - \frac{I_2(\kappa a)}{I_o(\kappa a)} \right) \right] - \frac{A_p \epsilon_w \psi_o \nabla P}{\mu} \left(\frac{I_2(\kappa a)}{I_o(\kappa a)} \right). \quad (2.83)$$

The term in square brackets on the righthand side is due to the contributions of electroosmotic flow and the conduction current, while the term on the far right is due to the applied pressure gradient. Setting the total current to zero, the streaming potential can be defined as

$$\left(\frac{E}{\nabla P} \right)_{sp} = \frac{\frac{\epsilon_w \psi_o}{\sigma_o \mu} \left(\frac{I_2(\kappa a)}{I_o(\kappa a)} \right)}{\left[1 + \frac{2\sigma_s}{a\sigma_o} + \frac{\epsilon_w^2 \kappa^2 \psi_o^2}{\sigma_o \mu} \left(\frac{I_1^2(\kappa a)}{I_o^2(\kappa a)} - \frac{I_2(\kappa a)}{I_o(\kappa a)} \right) \right]}. \quad (2.84)$$

This equation defines the electric field generated due to the streaming potential per Pascal/m of applied pressure. Neglecting the effects of surface conduction, the denominator will gradually tend to unity for large κa ratios, and thus the entire equation will tend towards $\frac{\epsilon_w \psi_o}{\sigma_o \mu}$, which will typically be quite small. For example, if the conductivity of the fluid is $30 \mu S$, the zeta potential is $40 mV$, the permittivity is $40 \epsilon_o$, and the viscosity is $5 \times 10^{-4} kg/(ms)$, the ratio of the electric field due to the streaming potential to the applied pressure gradient is approximately $950 \mu V/m/Pa$. The electroosmotic flow component generated from the streaming potential will therefore typically be negligible compared to the pressure driven flow. However, because electroosmotic flow is more efficient than pressure-driven flow in small pores, the streaming potential can become significant if the pore size is small.

Figure 2.8: Ratio of the electroosmotic volume flow induced by the streaming potential to the volume flow from an applied pressure gradient, for four different Debye lengths. A fluid conductivity σ_o of $30 \mu S$, a zeta potential ψ_o of $30 mV$, a permittivity ϵ_w of $61 \epsilon_o$, and a viscosity μ of $5 \times 10^{-4} kg/(ms)$ were used.

The ratio of the electroosmotic volume flow, induced by the streaming potential, to the pressure-driven volume flow (in the other direction) can be shown to be given by

$$\frac{U_{eo}}{U_P} = \left(\frac{\nabla P}{E} \right)_{cp} \left(\frac{E}{\nabla P} \right)_{sp}, \quad (2.85)$$

where $\left(\frac{\nabla P}{E}\right)_{cp}$ is given by equation 2.81 and $\left(\frac{E}{\nabla P}\right)_{sp}$ is given by equation 2.84. This is plotted in Figure 2.8 for a fluid conductivity σ_o of $30 \mu S$, a zeta potential ψ_o of $30 mV$, a permittivity ϵ_w of $61 \epsilon_o$, and a viscosity μ of $5 \times 10^{-4} kg/(ms)$, for four different κa ratios. It can be seen that the ratio of electroosmotic to pressure-driven volume flows approaches a maximum near a κa ratio of 1, indicating that the streaming potential is having its maximum effect for small κa ratios. For very small channels, the streaming potential can nearly prevent a net volume flow from flowing at all in the pores (a $\frac{U_{eo}}{U_P}$ ratio of one implies that the volume flow due to the streaming potential is equal to the volume flow due to the applied potential gradient). For larger pores, the streaming potential has less of an impact. This is because of the $1/a^2$ factor controlling the counter-pressure term $\left(\frac{\nabla P}{E}\right)_{cp}$ in equation 2.81 (i.e. the volume flow for pressure-driven flow is proportional to a^4 , while for electroosmotic flow it is proportional to a^2).

The streaming potential can therefore be seen to reduce the volume flow for pressure-driven flow if the pore size is small, especially for small κa ratios. This could have an impact on devices employing pressure-driven flow in porous materials, or employing electroosmotic flow to generate high pressures to force fluid through porous regions outside the electric field. For simplicity, streaming potential effects will not be considered in later sections. However, to be truly accurate, such effects will need to be considered in the future.

2.3 Electroosmosis in Porous Media

The classic model for electroosmotic flow in porous media is that of Overbeek [36, 23]. Overbeek began with Smoluchowski's result for the fluid velocity in a pore with a thin double layer (2.71):

$$u = -\frac{\epsilon_w \psi_o E}{\mu}. \quad (2.86)$$

In order to find the volume-averaged velocity of the fluid in a porous medium, Overbeek integrated over the interstitial volume of the bed:

$$\bar{u} = \frac{1}{V} \int_{\epsilon V} u dV = -\frac{\epsilon_w \psi_o}{\mu V} \int_{\epsilon V} E dV. \quad (2.87)$$

Overbeek further noted that, provided that the porous medium itself is non-conducting, the current can be found by

$$i = \sigma^* E = \frac{\sigma_o}{V} \int_{\epsilon V} E dV, \quad (2.88)$$

where σ^* is the conductivity in the porous medium, and σ_o the conductivity of the electrolyte solution. Combining these last two equations yields

$$\bar{u} = -\frac{\epsilon_w \psi_o}{\mu} \frac{\sigma^*}{\sigma_o} E. \quad (2.89)$$

According to Zeng et al [24], conductance of an open tube can be expressed as $\sigma_o A/L$, while for a porous medium, it is $\sigma_o A_e/l$. Using the relations in 2.2 and 2.4, the volume-averaged velocity can be expressed as

$$\bar{u} = -\frac{\epsilon}{\tau} \frac{\epsilon_w \psi_o}{\mu} E. \quad (2.90)$$

Since Overbeek's work, many authors have derived various relations for electroosmotic flow in porous media. Many assume, or demonstrate, the validity of Onsager's reciprocity theorem, which is based upon the thermodynamics of irreversible processes, and suggest that the cross-effect between electrical current flow and liquid transport is a symmetrical relationship [15]. The relationship between current and fluid flow is generally expressed as [15]

$$i = \sigma \cdot E - \chi \cdot \nabla P \quad (2.91)$$

$$\bar{u} = \beta \cdot E - \frac{K}{\mu} \cdot \nabla P \quad (2.92)$$

where χ and β are the electroosmotic coupling coefficient tensors. By Onsager's theorem, $\chi = \beta^T$, where T denotes the transpose operation.

Gross and Osterle [38] determined general relationships for nine different coupling

coefficients between fluid flow, solute flow, and current in ultrafine capillaries. All capillaries were considered identical, and only flow in individual capillaries was considered to determine the coupling coefficients. This model is known as the Space-Charge model, which has been modified many times in the literature.

Auriault and Strzelecki [39] derived general relationships using a homogenization method based upon an asymptotic expansion involving multiple scales. Their results suggest that, in general, cross-effects may not be symmetrical.

Basu and Sharma [40], two of the many authors to improve upon the Space-Charge model, attempted to take into consideration changes in solvent permittivity near the charged wall, ion hydration effects, finite ion sizes, and charge-regulating surface effects. In this model, it is assumed that the porous material consists of series of charged rods, with fluid flowing between them. This setup complicates the analysis of the potential distribution, as the contribution from numerous rods must be considered.

Levine and Neale analyzed electrophoresis and electroosmosis in a swarm of small spheres, taking into consideration the overlap of double layers, but only considering small surface potentials [41, 42, 43, 44]. Their analysis was extended by Kozak and Davis [45, 46, 44] for all surface potentials, taking into account double layer polarization as well, but neglecting double layer overlap of adjacent spheres. Lee was able to extend this theory to incorporate double layer overlap [47]. Similar analyses have been performed for fibrous porous media consisting of series of charged rods by Kozak and Davis [48], but are limited to low surface potential and do not take polarization into account. Ohshima derived analytical approximations for both swarms of spheres as well as fibrous porous media for the case of low surface potential [49, 50]. Lee once again was able to extend the theory for fibrous porous media to account for large potentials, double layer polarization, as well as double layer overlap [44].

Cwirko and Carbonnel used the method of spatial averaging to reduce the amount of numerical computation required in the Space-Charge model [51]. The method of spatial averaging breaks quantities such as the potential into the sum of an average

potential and the variation of the potential about the average. The resulting differential equations can be simplified using a number of assumptions, and solved using various closure schemes. Cwirko and Carbonnel remove the need to solve the Poisson-Boltzmann equation by this method. However, the model is still more complicated than desired for this study, and does not take into consideration boundary layers in the porous medium.

Coelho et al modelled electroosmosis in porous media with spatially periodic structures of different elements, randomly packed media, as well as reconstructed media, for small zeta potentials [15]. They sought coupling coefficients as described in equations 2.91 and 2.92. It was found that the electroosmotic coupling coefficient determined for media composed of periodic hollow circular capillaries worked very well for their simulation data for all structures; it also worked well when used in comparison with experimental data. However, in order to fit the data, it was necessary that an appropriate length scale, ξ , be chosen for the average pore size. They found the electroosmotic coupling coefficient for circular capillaries to be

$$\beta = \frac{8\epsilon_w\psi_o K}{\mu\xi^2} \left(\frac{2I_1(\kappa\xi)}{\kappa\xi I_o(\kappa\xi)} - 1 \right). \quad (2.93)$$

Ideally, $\xi = a$, but since the pore size can be difficult to estimate, an electrokinetic method was suggested as a way to measure ξ via the permeability through

$$K = \frac{\sigma^*}{\sigma_o} \frac{\xi^2}{8}. \quad (2.94)$$

Inserting equations 2.94 and using Zeng's scaling argument for the conductivity ratio [24], the coupling coefficient can be expressed as

$$\beta = \frac{\epsilon\epsilon_w\psi_o}{\tau\mu} \left(\frac{2I_1(\kappa\xi)}{\kappa\xi I_o(\kappa\xi)} - 1 \right). \quad (2.95)$$

Coelho et al found that, in order to better fit the data, it was necessary to modify the relationship in equation 2.94 to

$$K = \frac{\sigma^*}{\sigma_o} \frac{\xi^2}{12.5}. \quad (2.96)$$

All of the above models use Darcy-like expressions to model electroosmotic flow in porous media. Thus, they are incapable of incorporating viscous effects near boundaries or nonlinear effects at higher flow velocities. One attempt to incorporate boundary layer effects in porous media was made by Rathore and Horvath [23], who independently developed a model that could incorporate viscous effects near boundaries. The motivation behind their work was to investigate the effects of a mismatch in zeta potentials that often occurs in capillary electrochromatography (CEC), an analytical method that involves the use of glass tubes packed with porous or non-porous spheres. Electroosmosis is advantageous in such analytical techniques due to the flat velocity profile expected from electroosmosis relative to that in pressure-driven flow, and due to the possibility that electroosmosis can occur inside the porous spheres, where pressure-driven flow would not be possible due to the high pressures required. It is often found, in practice, that the zeta potential on the capillary wall is higher than that on the spheres, and thus, near the walls, a higher flow velocity may occur. It is therefore of importance to researchers in the CEC field to quantify the amount of dispersion that results.

Although they did not explicitly define it as such, Rathore and Horvath used a Brinkman expression to model the drag induced by the spheres on the liquid. In their model, they employed a permeability definition similar to that originally proposed by Burke and Plummer [25]. They noted that the drag on an individual sphere is given by Stokes' Law [25, 35], [52, p.303]

$$F_d = 6\pi\eta r_s u, \quad (2.97)$$

where r_s is the radius of the sphere. The total drag is then estimated by multiplying by the number density of spheres, defined by

$$N_{density} = \frac{\text{Solid Volume Fraction}}{\text{Volume of Sphere}} = \frac{1 - \epsilon}{\frac{4\pi}{3} r_s^3}. \quad (2.98)$$

The total drag force is then

$$F_{d_{tot}} = 6\pi\eta r_s u \left(\frac{1-\epsilon}{\frac{4\pi}{3}r_s^3} \right) = \frac{9}{2} \frac{\eta u (1-\epsilon)}{r_s^2}. \quad (2.99)$$

The drag force can be represented in terms of a Darcy permeability as

$$K = \frac{2}{9} \frac{r_s^2}{(1-\epsilon)}. \quad (2.100)$$

Note, however, that in their equations, Rathore and Horvath mistakenly used the solid particle diameter, d_p , instead of the radius of the sphere, r_s , in Stokes' Law (2.97) and in the equation for the number density of spheres (2.98), without adjusting it by a factor of two. This error has been replicated elsewhere in the literature (see, for example, Liapis and Grimes, [2]), but has been corrected in this work. To account for the fact that, in reality, the spheres are touching, and thus the total drag is not simply the sum of the drag on each individual sphere, a packing parameter, γ , was included. In terms of the solid particle diameter, their definition of permeability is thus

$$K = \frac{1}{18\gamma} \frac{d_p^2}{(1-\epsilon)}. \quad (2.101)$$

To account for the higher zeta potential at the capillary wall, they first considered the case where the spheres are uncharged, and thus the electroosmotic flow is due entirely to the charge at the walls. They assumed that the fluid velocity at the walls of the capillary, $r = R$, is given by Smoluchowski's equation (2.71), and is symmetric at $r = 0$. They then solved the equation

$$\frac{1}{r} \frac{d}{dr} \left(r \frac{du}{dr} \right) - \frac{u}{K} = 0, \quad (2.102)$$

which is a Brinkman equation. Noting the analogy between this and the linearized Poisson-Boltzmann equation in equation 2.72, the solution is given by

$$u(r) = u_{sw} \frac{I_o \left(\frac{r}{\sqrt{K}} \right)}{I_o \left(\frac{R}{\sqrt{K}} \right)}, \quad (2.103)$$

where u_{s_w} is given by Smoluchowski's equation, with $\psi = \psi_w$, the zeta potential at the wall. Thus, the velocity profile in a capillary with charged walls packed with uncharged spheres is analogous to the *potential* profile in an open capillary with charged walls. Thus, the velocity is highest at the walls, and very quickly goes to zero due to the drag on the fluid induced by the spheres. It can be seen, then, that in this case, electroosmotic flow occurs only in a very small region near the walls, the thickness of which is determined by the permeability.

In the case where the spheres also have a zeta potential associated with their surface, Rathore and Horvath added Smoluchowski's result with the above solution, but only considered the difference in zeta potential between the cylinder surface and the spheres' surface in the expression for u_{s_w} , i.e. $\psi = \psi_w - \psi_o$. Thus, their result is

$$u(r) = u_{s_w} \frac{I_o\left(\frac{r}{\sqrt{K}}\right)}{I_o\left(\frac{R}{\sqrt{K}}\right)} \left(1 - \frac{\psi_o}{\psi_w}\right) + u_{s_s}, \quad (2.104)$$

where u_{s_s} is again given by Smoluchowski's equation, but with $\psi = \psi_o$, the zeta potential of the spheres. This can be simplified to

$$u(r) = -\frac{\epsilon_w \psi_o E}{\mu} \left[1 + \frac{I_o\left(\frac{r}{\sqrt{K}}\right)}{I_o\left(\frac{R}{\sqrt{K}}\right)} \left(1 - \frac{\psi_w}{\psi_o}\right) \right]. \quad (2.105)$$

Rathore and Horvath's work is the first known attempt in the literature to incorporate viscous effects near boundaries into the model for electroosmotic flow in porous media. It can be seen that the permeability of the medium influences the size of the boundary layer near the wall. Thus, the permeability, K , can be considered to be a measure of the size of the boundary layer just as the Debye length is a measure of the double layer thickness. Although the theory in this thesis was derived independently from that of Rathore and Horvath, it will be seen that the models are similar.

Liapis and Grimes [2] have also developed models for electroosmotic flow in porous media intended specifically for CEC. Their model involves solving the Poisson-Boltzmann

equation numerically to find the velocity profile in individual pores, and integrating to find the average velocity in a single pore. Their model is therefore capable of handling thick double layers and high zeta potentials. In their model, the conductivity ratio $\frac{\sigma^*}{\sigma_o}$ was used as a fitting parameter to match their model with experiment. They assumed that this ratio was a measure of the tortuosity (in particular, they assumed that $\frac{\sigma^*}{\sigma_o} = \frac{1}{\sqrt{\tau}}$ in the notation used in this thesis), and selected $\tau \sim 2$ as a fitting parameter. They also incorporated Rathore and Horvath's model for mismatched zeta potentials, and thus their model represents one of the theories in the literature that is most relevant to this work.

In the next chapter, a model for electroosmotic flow in porous media will be developed using the generalized porous medium equation for fluid flow in porous media. This model will be seen to be consistent with the models of Overbeek [36], Coelho et al [15], Zeng et al [24], Rathore and Horvath [23], as well as Liapis and Grimes [2]. The model is capable of taking into consideration the viscous effects near solid boundaries, as in Rathore and Horvath's model, but is also capable of taking into consideration nonlinear effects at higher flow velocities as well as changes in porosity, and is capable of modelling flow in adjacent open and porous channels. Thus, the model that will be presented in this work will be seen to be consistent with other results in the literature, but is formulated in a more flexible framework that permits a diverse range of problems to be considered.

Chapter 3

Electroosmotic Flow in Porous Media

With the exception of Rathore and Horvath's model [23], models for electroosmotic flow in porous media take no account of viscous effects, and thus cannot be used to model microfluidic devices in which porous channels border open channels, the walls bounding the porous material have a different zeta potential than the porous material, or the porosity varies near the wall. Although the use of a viscous term was suggested by Rathore and Horvath [23], their model is not volume-averaged, and thus cannot easily be used to take into consideration changes in porosity, or to model adjacent porous and open channels, while still satisfying the requirement for conservation of mass. Furthermore, studies of pressure-driven flow in porous media have suggested that, at higher flow velocities, the drag on the fluid presented by the porous medium becomes nonlinear. It is possible that a similar effect exists for electroosmotic flow.

In this chapter, the generalized porous medium equation will be adapted for use in electroosmotic flow. This is the first electroosmotic flow model to capture all of the above effects. An effective charge density term will be derived that removes the dependence of the charge density on position, and is used to describe an effective electroosmotic force term in the generalized porous medium equation. The resulting model will be seen to be a combination of Darcy's Law, Brinkman's equation, and Forchheimer's equation for flow in porous media, and reduces to the Navier-Stokes equation when the porosity and tortuosity approach unity. Criteria are developed that can be used to determine the necessary conditions for Darcy's Law, Brinkman's equation, or Forchheimer's equation to apply.

To date, there has been little work on the effects of dispersion in electroosmotic flow. Models for dispersion in porous media are developed in Section 3.3, based upon dispersion models for pressure-driven flow. In particular, a Taylor-like analysis will be used to develop an effective Taylor dispersion coefficient due to the electroosmotic velocity profile in individual pores. This model will be seen to be consistent with a model developed by Griffiths and Nilson, using another technique [10]. A model for flow and dispersion in a heterogeneous medium, in which there is a statistical distribution of pore sizes, is then developed, and it is seen that the effective dispersion coefficient will depend upon the variance of the pore size distribution, and increases with time. It will be seen that the dispersion will typically be negligible for electroosmotic flow, but can be significant for pressure-driven flow. This is the first known model to take into account dispersion effects due to a distribution of pore sizes for electroosmotic flow.

3.1 The effective charge density approximation

In order to model electroosmotic flow at the scale of the porous medium, rather than at the scale of an individual pore, it is desirable to remove the charge density's dependence on position at the pore level. For pressure driven flow, the dependence on position of the flow profile was removed by assigning an effective permeability that was related to the volume flow through a single pore (see Section 2.1.3). A similar procedure will be used for electroosmotic flow. An effective, constant charge density will be obtained that results in the same volume flow as the actual charge density. This can be obtained by finding an equivalent pressure force that results in the same volume flow in an individual pore as in electroosmotic flow:

$$\nabla P_{eff} = -\rho_{eff}E = \rho_{eff}\nabla\phi. \quad (3.1)$$

The average volume flow due to a pressure gradient in a pore of arbitrary geometry was given in equation 2.16 as

$$U_{ave,P} = \frac{m^2}{k_o} \frac{\nabla P}{\mu} = \frac{m^2}{k_o \mu} \rho_{eff} E. \quad (3.2)$$

The average volume flow due to electroosmosis, extrapolating from equation 2.70, is

$$U_{ave,EOF} = \frac{\epsilon_w \psi_o E}{\mu} \left(\frac{\int \int \psi dA_p}{\psi_o A_p} - 1 \right), \quad (3.3)$$

where A_p is the cross-sectional area of an single pore. Setting the above two equations equal, and solving for the effective charge density results in the following:

$$\rho_{eff} = \frac{\epsilon_w \psi_o k_o}{m^2} \left(\frac{\int \int \psi dA_p}{\psi_o A_p} - 1 \right). \quad (3.4)$$

In the case of a medium composed of hollow capillaries, the pore shape factor, k_o , was 2, and the mean hydraulic radius, m , was $\frac{a}{2}$. If the wall potential is small, the linearized Poisson-Boltzmann solution for ψ can be used, resulting in (see equations 2.76 and 2.77)

$$\rho_{eff} = \frac{8\epsilon_w \psi_o}{a^2} \left(\frac{2I_1(\kappa a)}{\kappa a I_0(\kappa a)} - 1 \right). \quad (3.5)$$

Darcy's Law was given in equation 2.7 by

$$\bar{u} = -\frac{K}{\mu} \nabla P. \quad (3.6)$$

The permeability K , as defined in equation 2.26, is

$$K = \frac{\epsilon m^2}{\tau k_o}. \quad (3.7)$$

Darcy's law for electroosmotic flow in porous media, using the above relation for the permeability, the effective pressure gradient given by equation 3.1, and equation 3.4 for the effective charge density, is therefore

$$\bar{u} = \frac{\epsilon \epsilon_w}{\tau \mu} \psi_o E \left(\frac{\int \int \psi dA}{\psi_o A} - 1 \right), \quad (3.8)$$

where the $\frac{m^2}{k_o}$ dependence in each of the permeability and the effective charge density has cancelled. For double layers that are very thin relative to the pore radius, the integral will vanish, and Darcy's law for electroosmotic flow becomes

$$\bar{u} = -\frac{\epsilon\epsilon_w}{\tau\mu}\psi_o E, \quad (3.9)$$

which is independent of the pore geometry, as shown in several experimental studies [53, 54]. The effective charge density can alternatively be described in terms of the permeability of the medium, using equations 3.4 and 2.26, as

$$\rho_{eff} = \frac{\epsilon\epsilon_w\psi_o}{\tau K} \left(\frac{\int \int \psi dA_p}{\psi_o A_p} - 1 \right). \quad (3.10)$$

Equation 3.10 is the form of the effective charge density that will be used throughout this work. It should be noted that equation 3.9 is identical to Overbeek's result for EOF in porous media with thin double layers (2.90). Thus, this formulation is compatible with other results in the literature. Furthermore, an electroosmotic coupling coefficient, as in equation 2.92, can be defined, using the above equations, as

$$\beta = \frac{\rho_{eff} K}{\mu}. \quad (3.11)$$

For thin double layers, this results in

$$\beta = \frac{8\epsilon_w\psi_o K}{\mu a^2} \left(\frac{2I_1(\kappa a)}{\kappa a I_0(\kappa a)} - 1 \right). \quad (3.12)$$

which can be seen to be the same as Coelho's result (2.93), provided $a = \xi$.

3.2 The generalized porous medium equation for electroosmotic flow

Electroosmotic flow in porous media can be modelled more generally using the generalized porous medium equation (2.48), repeated here, but with the effective charge

density added to include the electroosmotic force on the fluid:

$$\frac{\sqrt{\tau}}{\epsilon} \frac{\partial \bar{u}}{\partial t} + \frac{\sqrt{\tau}}{\epsilon} \bar{u} \cdot \nabla \left(\frac{\bar{u}}{\epsilon} \right) = -\frac{\nabla P}{\sqrt{\tau} \rho_w} + \frac{\eta}{\sqrt{\tau}} \nabla^2 \left(\frac{\bar{u}}{\epsilon} \right) + g - \frac{\rho_{eff} \nabla \phi}{\sqrt{\tau} \rho_w} + F, \quad (3.13)$$

$$\nabla \cdot \bar{u} = 0, \quad (3.14)$$

$$F = -\frac{\eta_e \bar{u}}{K} - \frac{F_e \bar{u} |\bar{u}|}{\sqrt{K}}, \quad (3.15)$$

$$K = \frac{\epsilon^3 d_p^2}{36 k_o \sqrt{\tau} (1 - \epsilon)^2}, \quad (3.16)$$

$$F_e = \frac{1.75}{\sqrt{36 \epsilon^3 k_o \sqrt{\tau}}}, \quad (3.17)$$

$$\rho_{eff} = \frac{\epsilon \epsilon_w \psi_o}{\sqrt{\tau} K} \left(\frac{\int \int \psi dA_p}{\psi_o A_p} - 1 \right). \quad (3.18)$$

This model (equations 3.13 to 3.18) is the model that will be studied throughout the rest of this work. It represents the first model that is capable of modelling both electroosmotic and pressure driven flow, in porous and open channels, while taking viscous effects near boundaries as well as nonlinear effects at higher velocities into account. With a tortuosity of unity, and an effective charge density of zero, this model will reduce to the generalized porous medium equations of Vafai and Tien [27], and Nithiarasu et al [7]. If the porosity also approaches unity, this equation will reduce to the Navier-Stokes equations for flow in open channels.

It should be noted that the scaling used to derive the generalized porous medium equation includes the $\sqrt{\tau}$ factor for the applied pressure or voltage gradient outside of the permeability term, unlike Darcy's Law (compare, for example, equations 3.4 and 3.10 for the effective charge density). Although it is tempting to multiply equation 3.13 by $\frac{\sqrt{\tau}}{\epsilon}$, this should be avoided, as these factors are important in determining the relative importance of various terms in the equation.

By performing a dimensional analysis on the generalized porous medium equation,

it is possible to determine the relative importance of the different terms. Equation 3.13 can be made non-dimensional by setting $\bar{u} = Uu^*$, where u^* is a non-dimensional velocity of magnitude order 1 ($O(1)$), U is the dimensional magnitude of the velocity, and L is a characteristic dimension over which the velocity changes (usually defined by the smallest dimension of the medium). Assuming that the flow is steady, the generalized porous medium equation can then be rewritten as

$$\frac{\sqrt{\tau}}{\epsilon} \frac{U^2}{L} u^* \cdot \nabla \left(\frac{u^*}{\epsilon} \right) - \left(\frac{\eta}{\sqrt{\tau}\epsilon} \right) \frac{U}{L^2} \nabla^2 u^* + \frac{\eta_e U}{K} u^* + U^2 \frac{F_\epsilon u^* |u^*|}{\sqrt{K}} = \frac{1}{\sqrt{\tau} \rho_w L} (\nabla P + \rho_{eff} \nabla \phi). \quad (3.19)$$

As Darcy's Law is the traditional model for flow in porous media, the above equation will be rearranged so that the $\frac{\eta_e U}{K} u^*$ term will be $O(1)$. This yields

$$u^* + \frac{\sqrt{\tau}}{\epsilon} \frac{UK}{\eta_e L} u^* \cdot \nabla \left(\frac{u^*}{\epsilon} \right) - \frac{\eta}{\eta_e} \left(\frac{1}{\sqrt{\tau}\epsilon} \right) \frac{K}{L^2} \nabla^2 u^* + \frac{F_\epsilon U \sqrt{K}}{\eta_e} u^* |u^*| = \frac{\eta}{\eta_e} \frac{K}{\sqrt{\tau} \mu L U} (\nabla P + \rho_{eff} \nabla \phi). \quad (3.20)$$

The generalized porous medium equation is therefore seen to be governed by three different dimensionless numbers. The factor $\frac{\sqrt{\tau}}{\epsilon^2} \frac{UK}{\eta_e L}$ governing the $u^* \cdot \nabla u^*$ term can be interpreted as a modified Reynolds number. In open channels, the Reynolds number is defined as $Re = \frac{UL}{\eta}$, which is the ratio of inertial to viscous terms. At small Reynolds numbers, the viscous terms dominate, and the nonlinear momentum terms can be neglected. It is this viscous dominance that prevents mixing in microfluidic chips. At high Reynolds numbers, the nonlinear inertial terms dominate, and turbulent flow becomes a possibility. In porous media, the modified Reynolds number is

$$Re = \frac{\sqrt{\tau}}{\epsilon^2} \frac{UK}{\eta_e L}, \quad (3.21)$$

where the characteristic length is now determined by the ratio of the permeability, K , of the medium to the channel width, L . This takes into account the fact that the fluid is constricted by the very small pores through which it flows. Thus, for porous media, the modified Reynolds number will typically be very small, and the nonlinear inertial terms can be neglected. For example, the permeability, K , will usually be of $O(10^{-12})$ to $O(10^{-16})$, the velocity U will usually be of $O(10^{-3})$, the viscosity η will be of order 10^{-6} , and the characteristic length L will be $O(10^{-5})$ to $O(10^{-3})$. This

yields a modified Reynolds number of up to approximately 10^{-4} . It may be possible, however, that these terms will become significant in certain geometries at higher flow rates, due, for example, to singularities that occur for flow around a sharp corner.

Similarly, the viscous term $\nabla^2 u^*$ is governed by the dimensionless number $\frac{\eta}{\eta_e} \left(\frac{1}{\sqrt{\tau\epsilon}} \right) \frac{K}{L^2}$. The relative importance of the viscous term will be determined by the magnitude of the various factors in this dimensionless number, i.e. the ratio of the effective viscosity to the actual viscosity, the tortuosity and the porosity, the permeability, and the characteristic length scale, L . The dominant factor is the ratio $\frac{K}{L^2}$, which is also known as the *Darcy number*, D_a . It is defined by

$$D_a = \frac{K}{L^2}. \quad (3.22)$$

The square root of the permeability, $\sqrt{K}$, is usually used to define the characteristic length at the pore level. Thus, the Darcy number is proportional to the ratio of the size of the porous medium to the size of an individual pore. If $D_a \ll 1$, as is generally the case, then the $\eta \nabla^2 \bar{u}$ viscous term can be neglected. However, it may need to be considered if there are porosity or potential variations near a solid boundary, even if the Darcy number is small. This will be discussed below.

The nonlinear Forchheimer force term, $u^*|u^*|$, is governed by the dimensionless number $\frac{F_\epsilon U \sqrt{K}}{\eta_e} = \frac{\epsilon^2 F_\epsilon}{\sqrt{\tau}} \frac{R_e}{\sqrt{D_a}}$. Thus, a suitable condition to determine when the Forchheimer term can be neglected (relative to the Darcy u^* term) is given by

$$\bar{u} \ll \frac{\eta_e}{F_\epsilon \sqrt{K}}. \quad (3.23)$$

The F_ϵ factor is typically between 0.1 and 1. If, for example, the permeability K is $O(10^{-12}) \text{ m}^2/\text{s}$ and η_e is $O(10^{-6}) \text{ m}^2/\text{s}$, then $\bar{u}$ must be much less than 1 m/s in order to neglect the nonlinear term, which will typically be the case for microfluidic chips. As will be seen however, it is possible for the nonlinear term to become significant for flow velocities as small as a few mm/s if the porosity and pore size of the medium are large. This effect will most likely be seen in cases where electroosmotic and pressure-driven flow are used together to generate high flow rates.

If the flow is steady, and the modified Reynolds number and fluid velocity are small enough, the first two terms on the left hand side of 3.13 can be neglected, as well the nonlinear Forchheimer term in equation 3.15. The resulting equation is a variation of Brinkman's equation, for electroosmotic flow:

$$\frac{\eta}{\sqrt{\tau}} \nabla^2 \left(\frac{\bar{u}}{\epsilon} \right) - \frac{\eta_e \bar{u}}{K} = \frac{1}{\sqrt{\tau} \rho_w} (\nabla P + \rho_{eff} \nabla \phi). \quad (3.24)$$

This equation will be of interest when examining the effects of solid boundaries on the fluid velocity profile in a porous microchannel. A small boundary layer near the wall will develop, in which the fluid velocity goes to zero. In most cases, the Darcy number will be small, and this region can be neglected. The boundary layer will usually only be of interest if the device width is less than approximately twenty pore diameters. However, one must note that the volume averaging technique used to derive the generalized porous medium equation will no longer be valid if the Darcy number becomes too large. For example, in a channel that is only two pore widths wide, the flow profile calculated by the Brinkman equation will be a poor approximation of the actual profile.

The majority of situations in which the Brinkman equation will be of interest includes devices in which viscous effects near boundaries might become important, even though the Darcy number might be very small. Examples include devices that involve both open and porous sections, or devices where the walls surrounding the porous material have a different zeta potential than the porous material itself. It has also been found that the Brinkman equation can be more convenient than Darcy's Law, even in the case where the Darcy number is very small, as the formulation of Darcy's Law in some numerical simulators does not allow one to easily incorporate the electric force term.

If the Darcy number, D_a , is small, the Brinkman equation can be further simplified into a variation of Darcy's Law (with an additional electroosmotic force term) as

$$\frac{\eta_e \bar{u}}{K} = -\frac{1}{\sqrt{\tau} \rho_w} (\nabla P + \rho_{eff} \nabla \phi), \quad (3.25)$$

or

$$\bar{u} = -\frac{K}{\sqrt{\tau}\mu_e}(\nabla P + \rho_{eff}\nabla\phi), \quad (3.26)$$

where $\mu_e = \eta_e\rho_w$.

Finally, in the case where the Darcy number and the modified Reynolds number are both small, but the fluid velocity is not necessarily small (i.e. the Forchheimer velocity condition is not met), the generalized porous medium equation reduces to a Forchheimer equation:

$$\frac{F_\epsilon\bar{u}|\bar{u}|}{\sqrt{K}} + \frac{\eta_e\bar{u}}{K} = \frac{\nabla P + \rho_{eff}\nabla\phi}{\sqrt{\tau}\rho_w}. \quad (3.27)$$

The solution to this equation is given by

$$\begin{aligned} \bar{u} &= -\Lambda + \sqrt{\Lambda^2 - 2\frac{(\nabla P + \rho_{eff}\nabla\phi)K\Lambda}{\sqrt{\tau}\mu_e}}, \\ \Lambda &= \frac{\eta_e}{2F_\epsilon\sqrt{K}}. \end{aligned} \quad (3.28)$$

Noting that the second term in the square root sign is given by Darcy's Law for electroosmotic flow in equation 3.26, this can be rewritten as

$$\begin{aligned} \bar{u} &= -\Lambda + \sqrt{\Lambda^2 + 2\bar{u}_d\Lambda} \\ &= -\Lambda + \sqrt{(\Lambda + \bar{u}_d)^2 - \bar{u}_d^2}. \end{aligned} \quad (3.29)$$

where $\bar{u}_d$ is given by equation 3.26. If the first term in the square root is much greater than the second, which can be shown to be true if the Forchheimer velocity condition in equation 3.23 is satisfied, then the Forchheimer equation results in

$$\begin{aligned} \bar{u} &\approx -\Lambda + \sqrt{(\Lambda + \bar{u}_d)^2} \\ &\approx \bar{u}_d. \end{aligned} \quad (3.30)$$

Thus, the solution to the Forchheimer equation will be identical to that of Darcy's Law if the velocity is small, but appreciable differences will arise as the velocity approaches the Forchheimer velocity condition in equation 3.23. Thus, a critical velocity above

which the nonlinear Forchheimer drag effects must be considered could be (somewhat arbitrarily) defined by

$$\overline{u}_{crit} \approx 0.01 \frac{\eta_e}{F_\epsilon \sqrt{K}}. \quad (3.31)$$

Figure 3.1: Plot of the Forchheimer velocity for a few different porosity values. The velocity has been normalized with the Darcy velocity. The viscosity η_e was assumed to be $5 \times 10^{-7} \text{ m}^2/\text{s}$, the tortuosity was $\tau = 2$, and d_p was $1 \mu\text{m}$. Note that the x-axis has a logarithmic scale.

The Forchheimer fluid velocity as calculated using equation 3.29 is plotted in Figures 3.1 and 3.2 for a few different porosity and pore radius values, respectively. The fluid velocity has been normalized with respect to the Darcy velocity (3.26), which is the fluid velocity that would occur if the nonlinear drag effects in the Forchheimer force term (3.15) were neglected. Figure 3.2 is therefore a plot of the reduction in velocity caused by the nonlinear drag effects as a function of the expected Darcy velocity. The permeability and F_ϵ terms were calculated using equations 3.16 and 3.17, respectively. Increasing the porosity or pore radius reduces the critical velocity at which the Forchheimer term must be considered, although changes in the pore size will have a larger impact.

The dimensional analysis given above demonstrates that the generalized porous medium

Figure 3.2: Plot of the Forchheimer velocity for a few different pore radius values. The velocity has been normalized with the Darcy velocity. The viscosity η_e was assumed to be $5 \times 10^{-7} \text{ m}^2/\text{s}$, the porosity was $\epsilon = 0.4$, and the tortuosity was $\tau = 2$. Note that the x-axis has a logarithmic scale.

equation is a combination of Darcy's Law, the Brinkman equation, and Forchheimer's equation, and is therefore able to handle higher flow velocities as well as incorporate viscous effects at the boundaries. In most modelling problems, Darcy's Law will be sufficient. However, in some cases, such as devices incorporating both open and porous channels, charged walls, or combined pressure-driven and electroosmotic flow, the additional terms may become significant. Analytical solutions to the Darcy and Brinkman equations for a few simple geometries are given in the next chapter to help clarify some of the above discussion.

3.3 Dispersion in Porous Media

A fluid that is transported through a porous medium will be dispersed as it travels. For example, a solute plume that initially has a Gaussian concentration profile will experience band broadening, i.e., the Gaussian concentration profile will become wider as the solute travels through the medium. In many cases, the profile could become highly skewed, depending on the characteristics of the fluid velocity field. There are many possible sources of dispersion in a porous medium, such as the degree of

winding and connectivity of the pores, the velocity profile in the pores themselves, the macroscopic velocity profile in the porous medium, or the degree of homogeneity of the medium. In this section, some of these effects will be considered. However, it must be noted that dispersion in porous media is a very complicated phenomenon; only simple models will be outlined here. Due to the relatively flat profile of electroosmotic flow, as well as the relative independence of the velocity on the pore radius, it is expected that the dispersion in electroosmotic flow in porous media will be much smaller than that typically seen in pressure driven flow.

First, dispersion due to the electroosmotic flow profile in a single pore will be considered. The analysis will follow a similar analysis for pressure-driven flow by Taylor [8], and the result will be seen to be equivalent to another result derived independently in the literature using a different technique [10]. Then, models for flow and dispersion in heterogeneous media, in which the porous medium consists of a distribution of pore sizes, will be presented for what is believed to be the first time. These models are based upon models for dispersion in pressure-driven flow developed for groundwater flow [11, 12]. The models for electroosmotic flow and dispersion in heterogeneous media developed here will be used in Section 5.3, when microfluidic devices are built with nitrocellulose membranes, which are assumed to have a lognormal pore size distribution.

3.3.1 Taylor Dispersion due to EOF

The generalized porous medium equation uses a volume-averaging approach to determine the macroscopic velocity field in media of different geometries. However, no consideration of the velocity profile in each pore is taken, which can, as seen for the case of pressure-driven flow in section 2.1.5, have a major impact on the amount of dispersion seen by an analyte. For electroosmotic flow, this effect is expected to have a minimal impact, due to the flat, plug-like profile characteristic of electroosmotic flow. In this section, the effective diffusion coefficient for electroosmotic flow in a small cylindrical capillary of radius a is derived for the case of a low zeta potential. The final result will be found to be equivalent to another result derived independently in the literature [10].

The analysis presented here for electroosmotic flow is based upon that originally used by Taylor [8] for pressure-driven flow. The analysis focuses on the distribution of the flow velocity in the channel about the average velocity. It will be found that, in a reference frame that is moving with the average flow velocity, the analyte will be dispersed as if it is undergoing diffusion around the center of mass, allowing an effective diffusion coefficient to be derived.

The concentration of the analyte over time will be determined by the convection-diffusion equation, which is given by

$$D\nabla^2 C = \frac{\partial C}{\partial t} + u \cdot \nabla C, \quad (3.32)$$

where C is the concentration of the analyte and D is the diffusion coefficient. In cylindrical coordinates, assuming that C is symmetric about $r = 0$, this becomes

$$D \left(\frac{\partial^2 C}{\partial r^2} + \frac{1}{r} \frac{\partial C}{\partial r} + \frac{\partial^2 C}{\partial x^2} \right) = \frac{\partial C}{\partial t} + u(r) \frac{\partial C}{\partial x}. \quad (3.33)$$

In order to obtain an analytical solution to this equation, it will be assumed that the time required for effects due to convective transport to appear is much longer than the time required to reduce radial variations in concentration to a fraction of their original value [8]. It will also be assumed that the diffusion coefficient is independent of the concentration. The first assumption can be shown [8] to be valid so long as

$$\frac{L}{u_{ave}} \gg \frac{a^2}{3.8^2 D}, \quad (3.34)$$

where $\frac{L}{u_{ave}}$ is the time required for convection to have a significant effect on the concentration, assuming that the analyte is spread over a length of capillary, L . This is usually the case for systems of interest in this work. For example, if $a \simeq 1\mu m$ and $D \simeq 5 \times 10^{-9} \frac{m^2}{s}$, the time on the right hand side is $O(1 \times 10^{-5})s$. Thus, unless L is very small and/or u_{ave} is extremely fast, the assumption will be valid. Note, as well, that in Aris' analysis of dispersion in the more general case of a tube of arbitrary geometry [9], this condition can be further relaxed. The condition in (3.34) allows

equation 3.33 to be simplified to

$$D \left(\frac{\partial^2 C}{\partial r^2} + \frac{1}{r} \frac{\partial C}{\partial r} \right) = \frac{\partial C}{\partial t} + u(r) \frac{\partial C}{\partial x}. \quad (3.35)$$

This analysis will employ a change in the frame of reference by considering convection across a plane that moves with the average flow velocity, u_{ave} . It will be demonstrated that, in this reference frame, the analyte is dispersed as if it were undergoing diffusion relative to this moving plane of reference. The velocity in the pore is given by equation 2.76,

$$u(r) = u_o \left(\frac{I_o(\kappa r)}{I_o(\kappa a)} - 1 \right), \quad (3.36)$$

and the average velocity is found by dividing equation 2.77 by the cross-sectional area, A :

$$u_{ave} = u_o \left(\frac{2I_1(\kappa a)}{\kappa a I_o(\kappa a)} - 1 \right), \quad (3.37)$$

where

$$u_o = \frac{\epsilon_w \psi_o E}{\mu}. \quad (3.38)$$

Noting that the position x at time t is given by

$$x = u(r)t = u_o t \left(\frac{I_o(\kappa r)}{I_o(\kappa a)} - 1 \right), \quad (3.39)$$

and that the position x_1 with the new frame of reference is

$$x_1 = x - u_{ave}t = u_o t \left(\frac{I_o(\kappa r)}{I_o(\kappa a)} - \frac{2I_1(\kappa a)}{\kappa a I_o(\kappa a)} \right), \quad (3.40)$$

the velocity in this frame of reference, u_1 , will be given by

$$u_1 = \frac{x_1}{t} = u_o \left(\frac{I_o(\kappa r)}{I_o(\kappa a)} - f \right), \quad (3.41)$$

where f has been used to represent

$$f = \frac{2I_1(\kappa a)}{\kappa a I_o(\kappa a)}. \quad (3.42)$$

This allows equation 3.35 to be rewritten as

$$D \left(\frac{\partial^2 C}{\partial r^2} + \frac{1}{r} \frac{\partial C}{\partial r} \right) = \frac{\partial C}{\partial t} + u_o \left(\frac{I_o(\kappa r)}{I_o(\kappa a)} - f \right) \frac{\partial C}{\partial x_1}. \quad (3.43)$$

As pointed out by Taylor [8], since planes defined by $x_1 = \text{constant}$ have an average velocity of zero, any transfer of the analyte concentration, C , across these planes must be due entirely to the radial variation of C . If the condition in equation 3.34 is satisfied, this radial variation will disappear rapidly. The radial variation can then be calculated by

$$D \left(\frac{\partial^2 C}{\partial r^2} + \frac{1}{r} \frac{\partial C}{\partial r} \right) = u_o \left(\frac{I_o(\kappa r)}{I_o(\kappa a)} - f \right) \frac{\partial C}{\partial x_1}, \quad (3.44)$$

and $\frac{\partial C}{\partial x_1}$ can be assumed to be independent of r . The boundary condition for this problem requires that $\frac{\partial C}{\partial r} = 0$ at $r = a$, as the wall of the capillary is impermeable. Integrating twice with respect to r and applying this boundary condition results in

$$C = \frac{u_o}{D} \frac{\partial C}{\partial x_1} \left(\frac{I_o(\kappa r)}{\kappa^2 I_o(\kappa a)} - \frac{f r^2}{4} \right) + C_{x_1}, \quad (3.45)$$

where C_{x_1} sets the value of C at $r = 0$. The rate of transfer of C across the section at x_1 is given by

$$Q = 2\pi \int_0^a u_o \left(\frac{I_o(\kappa r)}{I_o(\kappa a)} - f \right) C r dr. \quad (3.46)$$

Inserting equation 3.45 into equation 3.46 and carrying out the details of the integration, the result is

$$Q = \frac{2\pi u_o^2 a^4}{D} \frac{\partial C}{\partial x_1} \left(-\frac{3f^2}{16} - \frac{f^2}{(\kappa a)^2} + \frac{f}{2(\kappa a)^2} + \frac{1}{2(\kappa a)^2} \right), \quad (3.47)$$

where the Bessel identity

$$\int_0^a I_o^2(\kappa r) r dr = \frac{a^2}{2} (I_o^2(\kappa a) - I_1^2(\kappa a)) \quad (3.48)$$

was used [55, p.203]. If the assumption in equation 3.34 is valid, $\frac{\partial C}{\partial x_1}$ is indistinguishable from $\frac{\partial C_m}{\partial x_1}$, where C_m is the mean concentration over a section [8]. Conservation

of mass requires that

$$\frac{\partial Q}{\partial x_1} = -\pi a^2 \frac{\partial C_m}{\partial t}. \quad (3.49)$$

Inserting equation 3.47 for Q , one obtains

$$D_{eff} \frac{\partial^2 C_m}{\partial x_1^2} = \frac{\partial C_m}{\partial t}. \quad (3.50)$$

This is seen to be a diffusion equation, and thus the mean concentration, C_m , is dispersed relative to a plane moving at the average velocity, u_{ave} , as if it were undergoing diffusion with a diffusion coefficient D_{eff} [8]. In this case, D_{eff} is given by

$$D_{eff} = \frac{u_o^2 a^2}{D(\kappa a)^2} \left(\frac{3f^2(\kappa a)^2}{8} + 2f^2 - f - 1 \right), \quad (3.51)$$

or, in terms of the Peclet number, $P_e = \frac{u_{ave} a}{D}$, with $u_{ave} = u_o(1 - f)$, the diffusion coefficient can be expressed as

$$D_{eff} = D \frac{P_e^2}{(1 - f)^2(\kappa a)^2} \left(\frac{3f^2(\kappa a)^2}{8} + 2f^2 - f - 1 \right). \quad (3.52)$$

Aris [9] was able to ease the restrictions placed on this type of analysis, and showed that, in general, the effective diffusion constant can be given by

$$D_{eff} = D (1 + \alpha P_e^2). \quad (3.53)$$

In this case α is given by

$$\alpha = \frac{1}{(1 - f)^2(\kappa a)^2} \left(\frac{3f^2(\kappa a)^2}{8} + 2f^2 - f - 1 \right). \quad (3.54)$$

It should be noted that a similar relation was derived independently by Griffiths and Nilson [10]. The two relations are identical, although the relation in equation 3.54 is in a slightly more convenient form because all Bessel functions are in the form of a ratio in the function f . Due to the exponential nature of modified Bessel functions, computation of modified Bessel functions with a large input parameter becomes difficult. However, with some approximations and a little manipulation, it

is possible to express ratios of Bessel functions in forms that can be easily computed numerically (see Appendix 7.2 for details).

Figure 3.3: Comparison of the effective diffusion coefficient for electroosmotic flow in a tube using α for different κa ratios. Also included is the α coefficient for pressure-driven flow.

The expression for α is plotted in Figure 3.3, where it is compared with the expression derived by Griffiths and Nilson [10]. It can be seen that the expression derived by Griffiths and Nilson can only be computed using the built-in Matlab Bessel functions up to about $\kappa a \approx 350$. However, in that range, the two expressions are equivalent. Also included for comparison in Figure 3.3 is $\alpha = 1/48$ for pressure-driven flow. It can be seen that the dispersion due to electroosmotic flow is less than that due to pressure-driven flow for all κa ratios.

An approximate expression for α for electroosmotic flow was derived by Griffiths and Nilson [10] that is within 2 percent of the actual expression over the entire range. It is given by

$$\alpha = \frac{4}{192 + 4(\kappa a)^{3/2} + 8(\kappa a)^2}. \quad (3.55)$$

Thus, the velocity profile at the pore scale can be taken into account through the

use of an effective diffusion coefficient. However, the Peclet number must be quite large for any significant dispersion to occur, unless the κa ratio is quite small. For large κa ratios, $\alpha \rightarrow 0$, and the effective diffusion coefficient approaches the actual diffusion coefficient of the analyte. In most cases, therefore, the effect of dispersion due to the individual pore profiles can be neglected for electroosmotic flow.

Note that the analysis included here only takes into consideration Taylor dispersion, and does not take into consideration dispersion induced by the porous nature of the medium itself. It is unknown at this time how studies such as that of Koch and Brady [35] for pressure-driven flow will apply to electroosmotic flow.

Macroscopic Taylor Dispersion

Taylor's theory of dispersion can also be used to model dispersion in porous channels due to velocity profiles at the macroscale. In this case, the effective diffusion coefficient using the above analysis would be used as the macroscopic diffusion coefficient, and the same type of analysis could be applied at the macroscopic level using the macroscopic velocity profile in order to obtain a new effective diffusion coefficient. Note that the Peclet number, P_e , will be different for the two different scales.

It was mentioned previously that the time required for convection to make an appreciable change in the concentration was of order $\frac{L}{u_{ave}}$. As stated above, the time required for a radial variation in C to die down to e^{-1} of its initial value is given by

$$t_c = \frac{a^2}{3.8^2 D}. \quad (3.56)$$

This allows one to introduce the concept of a *critical length*, L_c , as an estimate of the length of tube covered in this time. This can be expressed as

$$L_c > u_{ave} t_c = \frac{u_{ave} a^2}{3.8^2 D} = P_e \frac{a}{3.8^2}. \quad (3.57)$$

A similar analysis can be performed for flow in a two-dimensional rectangular channel of half-width b . Assuming that the analyte is carried along with the fluid (i.e. assuming that diffusion in the axial direction can be neglected), the diffusion equation

is of the form

$$D \frac{\partial^2 C}{\partial y^2} = \frac{\partial C}{\partial t}. \quad (3.58)$$

Using separation of variables and applying the boundary condition $\frac{\partial C}{\partial y}|_{y=b} = 0$ at the channel wall, the concentration of the analyte is given by the Fourier series

$$C(y, t) = \sum_{n=0}^{\infty} B_n \cos\left(\frac{2n+1}{2b}\pi y\right) e^{-(\frac{2n+1}{2b}\pi)^2 Dt} \quad (3.59)$$

where B_n is dependent upon the initial concentration profile. The time constant for this system can be estimated as

$$t_{crit} \approx \frac{4b^2}{\pi^2 D}. \quad (3.60)$$

This represents approximately the time it takes to reduce the variation in the concentration to 37 % of its initial value. This implies that a critical length can be defined by

$$L_{crit} > u_{ave} t_{crit} \approx u_{ave} \frac{4b^2}{\pi^2 D} = P_e \frac{4b}{\pi^2}. \quad (3.61)$$

This allows one to make a rough estimate as to how quickly a radial disturbance in concentration (introduced, for example, by turning a corner) can be eliminated.

The dispersion induced by a rounded corner can be estimated using the theory of Griffiths and Nilson [56, 57]. The dispersion for a square corner can be expected to be greater than that induced by a rounded corner, due to a dead zone near the outer turn. In some microfluidic designs, it may be of interest to ensure that channels after a corner or junction are of sufficient length to allow the concentration profile to smooth out. However, this will come at the expense of extra band broadening due to diffusion, and thus a trade-off would be required in practice.

3.3.2 Flow and Dispersion in Heterogeneous Porous Media

In many practical applications, the idealization of the porous medium as being composed of many tortuous, parallel capillaries of equal radius is a poor description of the actual medium. It is often more accurate to describe the medium in terms of a

statistical distribution of pore sizes. In practice, this distribution is often lognormal in shape. In pressure-driven flow, the velocity through each pore is proportional to the radius squared (a^2), while the volume flow through each pore is proportional to the radius to the power of four (a^4). This implies that the larger pores contribute much more to the total volume flow, and that the fluid in the smaller pores will fall far behind that residing in larger pores. This can lead to significant dispersion. In electroosmotic flow, however, the velocity through each pore is only dependent upon the zeta potential of the pore, provided that the κa ratio is large, resulting in much less dispersion.

Flow and dispersion in heterogeneous porous media is currently a highly active research topic in the soil sciences and in the oil industry, where plumes of solute are carried by groundwater flow over very large distances. A review of some of the complex theories developed to describe the stochastic flow fields involved can be found in the books by Dagan [58] or Gelhar [12]. In groundwater flow, the porous material, which could be, at any given position, any one of soil, sand, fractured rock, or clay, will vary with depth and with longitudinal distance, and will consist of a range of different grain sizes. In most microfluidic applications of interest, the porous material will be much less complicated. Hence, it will be assumed that the heterogeneous porous material will maintain statistical homogeneity- i.e. it will be assumed that a single pore size distribution will apply for the length of the device segment in question. In groundwater flow, this will often not be true, due to the vast length scales involved, but in microfluidic devices of a few millimeters in length, it is probably a reasonable assumption.

A conceptual illustration of a heterogeneous porous medium is given in Figure 3.4. The medium is composed of a distribution of different pore sizes and lengths. The process of dispersion is illustrated by the introduction of a flat concentration profile at time $t = t_1$, which has experienced a large amount of dispersion due to different flow speeds in each pore by time $t = t_2$. In a real porous medium, transverse diffusion across streamlines at junctions between pores will lower the amount of dispersion seen by an analyte. This effect is usually modelled using a correlation length L_h , which is a measure of the transverse distance between two molecules beyond which they

Figure 3.4: Conceptual illustration of a heterogeneous porous medium. The medium consists of pores of different sizes and lengths. An initially flat concentration profile at time $t = t_1$ is dispersed due to the different flow speeds in each pore, as seen at time $t = t_2$. The correlation length L_h is a measure of the transverse distance beyond which the velocities of two fluid molecules will no longer be correlated. This figure has been adapted from Gelhar et al [11].

are no longer correlated. This distance will depend upon the pore size as well as the interconnectedness of the pores themselves.

A simple model for dispersion in heterogeneous media will be implemented, following the treatment given for pressure driven flow in Chapter 5 of Gelhar [12]. Initially, the effects of diffusion across streamlines as well as the effects of the velocity profiles in individual pores will be neglected. Neglecting the effects of diffusion across streamlines is equivalent to assuming that the macroscopic Peclet number is high, as only the effects of convection are considered. As discussed previously, it is not difficult for the macroscopic Peclet number to become large; for example, if the channel width is 1 mm , the average flow speed is 0.5 mm/s , and the diffusion coefficient is $5 \times 10^{-9} \text{ m}^2/\text{s}$, the macroscopic Peclet number is 100.

The analysis in the previous section was based upon the distribution of the velocity profile in an individual pore about the mean. In this analysis, the variance of the average velocities in each pore about the average velocity of the pore size distribution will be used. First, the effective permeability and the effective charge density for the heterogeneous medium will be derived. Then, an effective dispersion coefficient will

be derived that is seen to be dependent on time. The effect that this time-dependent dispersion coefficient has on an analyte will then be modelled using a one-dimensional convection-diffusion equation. Specifically, breakthrough curves, in which the time required for the analyte to reach a specified position is plotted, will be used. It will be seen that if the variance of the pore size distribution is large, the analyte concentration profile becomes highly skewed, and it can take a long time for the bulk of the analyte to reach the specified position. However, the dispersion is much more severe in pressure-driven flow than in electroosmotic flow, as expected. The theory will then be modified to take into consideration the finding that pore size distributions in practice typically do not show evidence of pore sizes much larger than twice the average pore size, by using a truncated pore size distribution [59]. Finally, the effects of transverse diffusion will be taken into consideration, where it will be seen that the growth of the dispersion coefficient over time will asymptotically approach a constant effective dispersion coefficient that is dependent upon the variance of the pore size distribution. It will be seen that diffusion across streamlines due to transverse diffusion can significantly reduce the amount of dispersion predicted for an analyte.

As shown by Aris [9], the effective dispersion coefficient can be found in general to be equal to one half the rate of change of the variance of the concentration distribution. This can also be expressed as [12, 9]

$$\begin{aligned} D &= \frac{1}{2} \frac{d\sigma_{c_x}^2}{dt} = \frac{1}{2} \frac{d\sigma_{c_x}^2}{dX} \frac{dX}{dt} \\ &= \frac{u_{ave}}{2} \frac{d\sigma_{c_x}^2}{dX}, \end{aligned} \quad (3.62)$$

where $\sigma_{c_x}^2$ is the second moment of the concentration distribution with respect to position, X is the center of mass of the concentration distribution, and $u_{ave} = \frac{dX}{dt}$ is the intrinsic average fluid velocity.

Assuming that the flow is Darcian, the mean displacement of the concentration distribution can be given for the case of pressure driven flow as

$$X_P = \mathbf{E}[x] = u_{ave}t = \frac{\overline{K}}{\epsilon\mu_e} \nabla P t, \quad (3.63)$$

where the fact that $u_{ave} = \overline{u} \frac{\sqrt{\tau}}{\epsilon}$ has been used. The $\mathbf{E}[\cdot]$ notation denotes the expected value of the variable in question with respect to a given pore size distribution. The average permeability, $\overline{K}$, represents the expected permeability, weighted by the volume flow in each pore, and will be defined more formally shortly. For electroosmotic flow, the mean displacement of the concentration distribution can be found by

$$X_{EOF} = \mathbf{E}[x] = u_{ave}t = \frac{\overline{K\rho_{eff}}}{\epsilon\mu_e} \nabla\phi t. \quad (3.64)$$

It has been assumed implicitly in equations 3.63 and 3.64 that only the permeability, K , and the effective charge density, ρ_{eff} , depend upon the pore size distribution. The variance of the displacement of the concentration distribution for pressure driven flow can be found by [12]

$$\begin{aligned} \sigma_{c_{xP}}^2 &= \mathbf{E}[(x - X_P)^2] = \mathbf{E}[(K - \overline{K})^2] \left(\frac{\nabla Pt}{\epsilon\mu_e} \right)^2 \\ &= X_P^2 \left(\frac{\sigma_K^2}{\overline{K}^2} \right), \end{aligned} \quad (3.65)$$

where σ_K^2 is the variance of the permeability. For electroosmotic flow, the variance of the displacement is

$$\begin{aligned} \sigma_{c_{xEOF}}^2 &= \mathbf{E}[(x - X_{EOF})^2] = \left(\frac{\nabla\phi t}{\epsilon\mu_e} \right)^2 \mathbf{E}[(K\rho_{eff} - \overline{K\rho_{eff}})^2] \\ &= X_{EOF}^2 \left(\frac{\sigma_{K\rho_{eff}}^2}{\overline{K\rho_{eff}}^2} \right), \end{aligned} \quad (3.66)$$

where $\sigma_{K\rho_{eff}}^2$ is the variance of the product of the permeability and the effective charge density. The effective diffusion constant can be found for each case using equation 3.62. For pressure driven flow, this results in

$$\begin{aligned} D_{h_P} &= \frac{u_{ave}}{2} \frac{d\sigma_{c_{xP}}^2}{dX} = u_{ave} X_P \left(\frac{\sigma_K^2}{\overline{K}^2} \right) \\ &= u_{ave}^2 t \left(\frac{\sigma_K^2}{\overline{K}^2} \right), \end{aligned} \quad (3.67)$$

while for electroosmotic flow, the effective dispersion coefficient is

$$\begin{aligned} D_{h_{EOF}} &= \frac{u_{ave}}{2} \frac{d\sigma_{c_{xEOF}}^2}{dX} = u_{ave} X_{EOF} \left(\frac{\sigma_{K\rho_{eff}}^2}{K\rho_{eff}^2} \right) \\ &= u_{ave}^2 t \left(\frac{\sigma_{K\rho_{eff}}^2}{K\rho_{eff}^2} \right). \end{aligned} \quad (3.68)$$

It can be seen that the effective longitudinal dispersion coefficient in both cases increases linearly with time. The rate of increase of the dispersion coefficient is proportional to the square of the average velocity for the distribution. It is also proportional to the extent of the variation of permeability about its mean value for pressure driven flow, and the variation of the product of the permeability and effective charge density about its mean value for electroosmotic flow. In order to calculate these parameters, the statistical distribution of pore sizes must be known. The effect of a time-dependent dispersion coefficient on the concentration distribution over time will be considered below for the case of a lognormally distributed pore size distribution.

Dependence of K , ρ_{eff} , and u_{ave} on the Pore Size Distribution

As mentioned earlier, many porous materials of interest exhibit a pore size distribution that is lognormal in shape. A convenient form for the pore radius lognormal probability density function that was recommended by Zydney et al [60,61] is

$$p_a(a) = \frac{1}{a\sqrt{2\pi d}} \exp^{-\frac{(\ln(\frac{a}{M}) + \frac{d}{2})^2}{2d}}, \quad (3.69)$$

where M is the distribution mean and d can be defined in terms of the mean and pore size standard deviation σ_a as

$$d = \ln \left[1 + \left(\frac{\sigma_a}{M} \right)^2 \right]. \quad (3.70)$$

This form is convenient as it is expressed in terms of the distribution mean and standard deviation. If the most probable pore size (the peak of the distribution), M_p ,

is known, rather than the actual distribution mean, M , the two can be related by

$$M_p = M \left[1 + \left(\frac{\sigma_a}{M} \right)^2 \right]^{-\frac{3}{2}}. \quad (3.71)$$

The average permeability of the medium for pressure driven flow can be found by weighting the expected value of the permeability by the cross-sectional area of the pore and dividing by the expected value of the pore cross-sectional area, as follows:

$$\bar{K} = \frac{\int_0^\infty K \pi a^2 p_a(a) da}{\int_0^\infty \pi a^2 p_a(a) da}. \quad (3.72)$$

The variance of the permeability, σ_K^2 , can then be calculated as

$$\begin{aligned} \sigma_K^2 &= \mathbf{E}[(K - \bar{K})^2] \\ &= \int_0^\infty (K - \bar{K})^2 p_a(a) da. \end{aligned} \quad (3.73)$$

For electroosmotic flow, it is the product of the effective charge density and the permeability that must be averaged:

$$\overline{K \rho_{eff}} = \frac{\int_0^\infty K \rho_{eff} \pi a^2 p_a(a) da}{\int_0^\infty \pi a^2 p_a(a) da}. \quad (3.74)$$

Its variance can be found as

$$\begin{aligned} \sigma_{K \rho_{eff}}^2 &= \mathbf{E}[(K \rho_{eff} - \overline{K \rho_{eff}})^2] \\ &= \int_0^\infty (K \rho_{eff} - \overline{K \rho_{eff}})^2 p_a(a) da. \end{aligned} \quad (3.75)$$

Using these definitions, it is possible to construct a Darcy model for electroosmotic flow in heterogenous media (3.26), using the average permeability $\bar{K}$ instead of K for pressure-driven flow, and using $\overline{K \rho_{eff}}$ instead of the individual terms K and ρ_{eff} for electroosmotic flow. It must be stressed that in general, however, $\overline{K \rho_{eff}} \neq \bar{K} \bar{\rho_{eff}}$. This complicates the modelling of heterogeneous media using the generalized porous

medium equation, as ρ_{eff} and K appear in different terms (i.e. not in the form of a product). However, noting that the a^2 dependence on each of the effective charge density and permeability cancels in their product (see, for example, equation 3.8), this problem can be surmounted by redefining the effective charge density and the permeability in heterogeneous media in terms of the average pore size as follows:

$$\rho_{effh} = -\frac{8\epsilon_w\psi_o}{M^2} \quad (3.76)$$

$$K_h = \frac{\epsilon M^2}{8\sqrt{\tau}} \frac{\int_0^\infty |f_{\kappa a}(\kappa a)| \pi a^2 p_a(a) da}{\int_0^\infty \pi a^2 p_a(a) da}, \quad (3.77)$$

where $f_{\kappa a}(\kappa a)$, the dependence of the effective charge density on the pore size due to double layer effects, has been used to modify the permeability of the heterogeneous medium. For pores with small zeta potentials, $f_{\kappa a}(\kappa a)$ is (see equation 3.5)

$$f_{\kappa a}(\kappa a) = \left(\frac{2I_1(\kappa a)}{\kappa a I_0(\kappa a)} - 1 \right). \quad (3.78)$$

With this modification, the generalized porous medium equation will reduce to the Darcy model used in this section for flow in heterogeneous media, provided, of course, the modified Reynolds number and the Darcy number are small enough.

In order to better understand how the variance (σ_a^2) and mean (M) of the distribution will impact the total dispersion of an analyte, the dependence of the permeability, K , the effective charge density, ρ_{eff} , and the average velocity, u_{ave} , on the pore size distribution will be analyzed in detail for a lognormal pore size distribution, for both pressure-driven and electroosmotic flow.

In the case of pressure driven flow, the extent of the dispersion induced by a log-normal pore size distribution will largely depend upon the distribution variance, σ_a^2 . Figure 3.5 illustrates two different pore size distributions along with a plot of the permeability as a function of pore size. If the variance is large, it can be seen that larger pore sizes will have more of an impact on the total permeability. The average velocity in the pore is proportional to the permeability, and thus there will be more

(a) $M = 0.1 \mu m$, $\sigma_a = 0.1 \mu m$ (b) $M = 1 \mu m$, $\sigma_a = 0.2 \mu m$

Figure 3.5: Comparison of two different lognormal pore size distributions and the permeability as a function of pore size. Both the permeability and the pore radius distribution have been normalized to facilitate comparison.

(a) $M = 0.1 \mu m$, $\sigma_a = 0.1 \mu m$ (b) $M = 1 \mu m$, $\sigma_a = 0.2 \mu m$

Figure 3.6: Comparison of two different lognormal pore size distributions and the average volume flow in pressure driven flow as a function of pore radius. Both the average volume flow and the pore radius distribution have been normalized to facilitate comparison. Note that the average volume flow has the same functional form as the permeability.

dispersion due to the larger velocity contributions from the larger pores (see Figure 3.6).

Figure 3.7: Comparison of two different lognormal pore size distributions and the effective charge density as a function of pore size. The pore radius distribution has been normalized with respect to the effective charge density in each case to facilitate comparison. The Debye length in this case is 5 nm.

The amount of dispersion in electroosmotic flow will depend upon both the distribution variance, σ_a^2 , and the mean pore size, M , due to double layer effects if the pore size is small. The effective charge density as a function of pore size is illustrated in Figure 3.7 for two different pore size distributions, using a Debye length of 5 nm. It has been assumed here that the zeta potentials are small enough to use the linearized solution to the Poisson-Boltzmann equation (2.58). In the left hand plot (Figure 3.7(a)), the variance is large relative to the mean pore size, while the mean pore size is small enough for double layer effects to be significant, and thus the effective charge density varies substantially over the pore size distribution. In the right hand plot (Figure 3.7(b)), the mean pore size is much larger, greatly reducing the double layer effects, while the variance is a much smaller fraction of the mean pore size, so the effective charge density varies less over the pore size distribution. The different extents to which the fluid velocity varies over the two different pore size distributions can be clearly seen in Figure 3.8. The average velocity varies little at all over the pore size

Figure 3.8: Comparison of two different lognormal pore size distributions and the average volume flow in electroosmotic flow as a function of pore size. Both the average volume flow and the pore radius distribution have been normalized to facilitate comparison. The Debye length in this case is 5 nm.

distribution with the larger mean pore size (3.8(b)), but has a large variation over the distribution with the smaller pore size (3.8(a)).

Breakthrough Curves for Heterogeneous Porous Media

It was found that the effective dispersion coefficient was dependent upon time, and related to the variance of the pore size distribution. The effect that a time-dependent dispersion coefficient will have on a concentration distribution will now be considered in a one dimensional model. Analytical solutions to the convection-diffusion equation with time-dependent coefficients were found by Marinoschi et al [62] for one, two, and three dimensional problems. For the one dimensional case, the solution is of the form

$$C(t, x) = \frac{C_o}{\sqrt{4\pi\tilde{t}}} \exp \left[-\frac{(x - u_{ave}t)^2}{4\tilde{t}} \right], \quad (3.79)$$

where $\tilde{t}$ is given by

$$\tilde{t} = \int_0^t D(\tau) d\tau. \quad (3.80)$$

In the case considered here, $D = D_h$ is a linear function of time, given either by equation 3.67 or 3.68, which implies that $\tilde{t} = D_h t/2$. The solution to the convection-diffusion equation then becomes

$$C(t, x) = \frac{C_o}{\sqrt{2\pi D_h t}} \exp \left[-\frac{(x - u_{ave} t)^2}{2 D_h t} \right]. \quad (3.81)$$

This equation can be used to visualize the effects of a time-dependent dispersion coefficient over time.

Figure 3.9: Comparison of the breakthrough curves at different positions for two different lognormal pore size distributions for pressure driven flow. All concentration profiles have been normalized with the first concentration profile in each plot.

The impact of variations in velocity on the concentration profile over time can be visualized by plotting the breakthrough curves for each case. A breakthrough curve is a plot of the amount of analyte that arrives at a given fixed location over time. The breakthrough curves for each case can be obtained by plotting the solution to the convection-diffusion equation, given by equation 3.81, at a fixed x position downstream from the initial concentration distribution. The breakthrough curves for pressure driven flow are shown in Figure 3.9 for four different positions. It can be seen that there is significant dispersion for both pore size distributions. The analyte does not

reach the designated position all at once, but instead the concentration rises quickly, due to the arrival of the faster-flowing fluid in the larger pores, and exhibits a long tail as the slower-moving fluid from the smaller pores gradually reaches the designated position. It is evident from the plots that the amount of dispersion increases over time, as expected.

Figure 3.10: Comparison of the breakthrough curves at different positions for two different lognormal pore size distributions for electroosmotic flow. All concentration profiles have been normalized with the first concentration profile in each plot.

The dispersion in pressure-driven flow can be contrasted with that of electroosmotic flow using the breakthrough curves for the same pore size distributions in Figure 3.10. It can be seen that for the larger average pore size, there is virtually no dispersion, as nearly all the analyte arrives at the same time (the average velocity in each pore will be independent of pore size if the pore size is much larger than the double layer thickness). For the smaller average pore size, it can be seen that there can be significant delays before all of the analyte arrives, due to double layer effects. This demonstrates the importance of carefully selecting the properties of the porous medium if dispersion is a concern. Although the dispersion in electroosmotic flow is less than that seen in pressure-driven flow in both cases, an improvement in performance may be possible if the pore size distribution contains very few pores in the range in which double layer

effects must be considered. It will be seen later that, if transverse diffusion is taken into consideration, the dispersion caused by double layer effects when the average pore size is small can usually be neglected.

Figure 3.11: Comparison of the breakthrough curves at different positions for a transport process that is time dependent and regular transport for electroosmotic flow. All concentration profiles have been normalized with the first concentration profile in each plot.

A comparison of the time-dependent dispersion process with a process that is not time-dependent is illustrated in Figure 3.11. It can be seen that the process involving constant coefficients (i.e. regular diffusion) results in Gaussian profiles, while in the time-dependent model used here, the profiles can be highly skewed. The diffusion constant for the normal diffusion case was arbitrarily chosen to be $5D_{h_{EOF}}/t$ (the $1/t$ was required to remove the time dependency of $D_{h_{EOF}}$), while the dispersion coefficient for the time-dependent model was $D_{h_{EOF}}$ (since the model for electroosmotic flow was used).

Truncated Pore Size Distributions

In practice, it is often found that it is rare for porous materials to have a maximum pore size, a_{max} , more than twice the average pore size, M [59]. Porous membranes

used in filter applications are often specified in terms of their maximum pore size. Thus, some porous materials might be better modelled using a truncated probability distribution for the pore size. The probability density function for the lognormal distribution defined previously is strictly defined on the interval $[0, \infty]$. In the figures illustrated here, the integration was carried out using a maximum pore size that was much larger than the average pore size, so as to approximate an integration to infinity. However, if $a_{max} < 2M$, this strategy is longer possible. A truncated distribution function that still has an area of one was defined by Bowen and Welfoot as [59]:

$$p'_a(a) = \frac{p_a(a)}{\int_0^{a_{max}} p_a(a)}. \quad (3.82)$$

The truncated distribution function $p'_a(a)$ can then replace $p_a(a)$ in the above expressions. In general, this will result in a slightly lower permeability and average velocity, due to the smaller impact of the largest pores.

Figure 3.12: Plot of the parameter $\omega = \frac{\sigma_K^2}{K^2}$ over a range of σ_a/M ratios for pressure driven flow. $M = 1\mu m$.

As seen in equations 3.67 and 3.68, the dispersion due to the heterogeneity of the media for both pressure and electroosmotic flow is of the form $D_h = \omega u_{ave}^2 t$, where ω is the ratio of the variance to the square of the mean, and is given by the term in brackets in either of the above two equations (3.67 or 3.68). The extent of the dispersion for a given flow velocity will be largely determined by the parameter ω , which

Figure 3.13: Plot of the parameter $\omega = \frac{\sigma \kappa \rho_{eff}^2}{K \rho_{eff}^2}$ over a range of σ_a/M ratios for electroosmotic flow for two different κM ratios.

is ultimately controlled by the pore size variance. In Figure 3.12, the parameter ω is plotted over a range of σ_a/M ratios for pressure driven flow, using two different values of a_{max} , $a_{max} = 40M$ and $a_{max} = 2M$, where the larger limit is meant to simulate an infinite distribution. It can be seen that as the pore size variance increases, the dispersion increases. However, the dispersion effects are not as severe if the pore size distribution is truncated closer to the average pore size M .

The parameter ω is plotted in Figure 3.13 for electroosmotic flow for two different κM ratios. For a large κM ratio (see Figure 3.13(a)), the Debye layer effects are negligible, and very little dispersion occurs. However, for a smaller κM ratio (see Figure 3.13(b)), the dispersion is more severe. It is interesting to note that a truncated distribution results in more dispersion if the κM ratio is large, as the smaller pores play a larger role in determining the overall dispersion. This is the opposite of what occurs in pressure-driven flow. For small κM ratios, the behaviour of ω is more complicated. For small variances, the truncated pore size distribution has less dispersion, as the larger pores (up to $a_{max} = 2M$), for which the κa ratios are large, play a larger role in determining the overall dispersion. However, for larger variances, the larger pores have no additional effect as pores larger than $2M$ are cut off by the

truncated distribution, and the dispersion once again becomes larger than that for a non-truncated distribution.

Effects of Transverse Diffusion

It must be noted that the contribution to the total dispersion due to the heterogeneity of the media, D_h , has been found by neglecting transverse diffusion (diffusion perpendicular to the direction of flow). It is expected that the dispersion predicted using the above model will exaggerate the amount of dispersion that would actually occur, as transverse diffusion would tend to cause more mixing between streamlines at pore junctions. This would cause an analyte in the faster pores to diffuse into the slower pores, and vice versa. The diffusion of analyte across streamlines will therefore limit the extent of the dispersion, and in fact would eventually yield a Gaussian process, where the dispersion coefficient is once again constant. More advanced models, such as that of Gelhar et al [11, 12] or Dagan et al [63, 64, 58] could be used as a starting point to model these effects. An estimate of the time required for the dispersion process to once again become Gaussian could be estimated using equation 30 of Gelhar et al [11], which resulted from a Taylor dispersion-like analysis of flow in a stratified aquifer:

$$D_h(v) = D_{h\infty} \left[(1 + e^v((2v+1)^2 - 2)\text{erfc}(\sqrt{v})) - 2\sqrt{\frac{v}{\pi}}(2v+1) \right]. \quad (3.83)$$

Here, $D_{h\infty}$ is the asymptotic value for the heterogeneous dispersion coefficient for large time. It is given by

$$D_{h\infty} = \frac{\omega}{3} \frac{L_h^2 u_{ave}}{D_t}, \quad (3.84)$$

where D_t is the diffusion (or dispersion) coefficient in the transverse direction, and L_h is a typical length scale of the heterogeneous medium. L_h is usually defined by a correlation length, i.e. a distance between two points beyond which fluid velocities are no longer correlated. One estimate of L_h could then be defined as the maximum pore diameter, or $L_h = 2a_{max}$. In reality, the correlation length L_h will depend on the interconnectedness of the porous medium, as diffusion across streamlines can only allow mixing between pores at the junctions between pores. The parameter v in

equation 3.83 is dependent upon time, and is given by

$$v = \frac{Dt}{L_h^2}. \quad (3.85)$$

For small times, equation 3.83 will reduce to the D_h values derived above. For larger times, it will approach the asymptotic value given by $D_{h\infty}$. A plot of D_h over time for pressure driven flow is given in Figure 3.14 for two different pore size distributions and flow velocities. It can be seen that for the example with larger pores and a faster flow velocity (Figure 3.14(a)), it takes over 1000 seconds to reach the asymptotic value, and the asymptotic value is almost 3000 times the diffusion coefficient. For the example with smaller pores (Figure 3.14(b)), it takes less than a second to reach the asymptotic value, which is negligible compared to the diffusion coefficient. The predictions of the 1D model are shown for comparison; it can be seen that the 1D model can greatly overestimate the dispersion coefficient over time.

Figure 3.14: Plot of D_{hp} over time using equation 3.83 for two different pore distributions and flow velocities. The values $D_t = 0.1 \times 10^{-9} m^2/s$, $\epsilon = 0.4$, $\tau = 1.9$, and $L_h = 2a_{max}$ were used.

It is, therefore, apparent that for membranes with a small mean pore size, the effects of transverse diffusion will remove much of the dispersion caused by the heterogeneity of

the medium. This is particularly beneficial for electroosmotic flow, as dispersion was caused mostly in the small pores due to double layer overlap. However, for pressure-driven flow, at higher flow velocities and for larger pore sizes, the asymptotic value for the dispersion coefficient can become quite large, and take a long time to be reached. It must also be noted that for many analytes of interest, such as DNA, the diffusion coefficients can be much lower than those used here, which could considerably increase the amount of dispersion seen by the analyte.

Taylor Dispersion in Heterogeneous Porous Media

It was shown previously in Section 3.3.1 that the velocity profiles in individual pores will lead to an effective Taylor dispersion coefficient of

$$D_{eff} = D (1 + \alpha P_e^2). \quad (3.86)$$

In heterogeneous porous media, the average effective Taylor dispersion coefficient that takes into consideration the pore size distribution must be found. The total dispersion in the medium, D_{tot} , could then be found by

$$D_{tot} = D_h + \mathbf{E}[D_{eff}] = D + D_h + D \int_0^\infty \alpha P_e^2 p_a(a) da, \quad (3.87)$$

where both the pore scale Peclet number, P_e , and the constant α depend on the pore size, a . Once again, the pore scale Peclet number is given by $P_e = \frac{u_{ave} a}{D}$. For pressure driven flow the average velocity is given by

$$u_{ave} = \frac{a^2}{8} \frac{\nabla P}{\sqrt{\tau} \mu}, \quad (3.88)$$

while α is given by 1/48. For electroosmotic flow, the average velocity is given by equation 3.37, while α is given by equation 3.54. Once again, however, as the pore scale Peclet numbers will typically be small, the contribution due to Taylor dispersion can usually be neglected. The total dispersion will in that case be found by

$$D_{tot} = D_h + \mathbf{E}[D_{eff}] = D + D_h. \quad (3.89)$$

3.4 Conclusion

In this chapter, the model for electroosmotic flow in porous media was formulated. This is the first known attempt to describe velocity profiles due to electroosmotic flow in porous media generically. It was seen that the generalized porous medium equation reduces to Brinkman's equation and Darcy's Law, and thus enables modelling in many different types of media without needing to change equations. It was seen that the classical results in the literature for electroosmotic flow in porous media can be reproduced in the Darcy approximation. This model has the advantage of being capable of modelling both pressure-driven and electroosmotically-driven fluids, and thus the design of microfluidic circuits taking advantage of both techniques can be modelled simultaneously.

The model developed here relies heavily on an accurate estimation of the permeability K and the effective charge density, ρ_{eff} . These two parameters are essential in transforming the problem from the microscale to the macroscale. Different definitions of the permeability from the literature can easily be incorporated into the model. Although the effective charge density model used here does not consider effects such as the polarization of the double layer, these effects can be incorporated in the future simply by redefining the equation for electroosmotic volume flow in a unit cell of the porous medium (equation 3.3), and setting it equal to the volume flow due to a pressure gradient, as outlined in the beginning of section 3.1. In this way, the effective charge density and permeability could become tensors to incorporate anisotropic effects.

The velocity profiles in individual pores can be taken into consideration by defining an effective diffusion coefficient, as described in section 3.3.1. Taylor dispersion can also be used at the macroscale to model, for instance, band spreading around a rounded corner, allowing one to approximate more complicated microfluidic circuits with relatively simple models. However, the generalized porous medium equation could be used to analyze such circuits in much more detail, and permits the analysis of flow profiles around, for example, rectangular corners, which can be more practical in many situations.

A simple model for electroosmotic and pressure-driven flow in heterogeneous porous media was also developed. By neglecting the effects of transverse diffusion, a dispersion coefficient that is linearly proportional to time was derived, resulting in skewed breakthrough curves that are dependent upon the variance of the pore size distribution for the medium. This is the first known model that can produce breakthrough curves for electroosmotic flow in heterogeneous porous media. The use of more sophisticated models that incorporate transverse diffusion effects, which permit the diffusion of solute across streamlines, will result in a dispersion coefficient that asymptotically approaches a constant value. The approach to the asymptotic value can be extremely fast for media with a small average pore size, but slow for media with larger average pore sizes. An accurate estimate of the approach to the asymptotic value will ultimately depend on the degree of interconnectedness of the pores.

The models developed here will be implemented in the next few chapters, to demonstrate how they may be used to model different phenomena of interest in microfluidic devices incorporating porous media.

Chapter 4

Analytical Solutions for EOF

In the previous chapter, the generalized porous medium equation was proposed as a general framework for modelling electroosmotic and pressure-driven flow in porous media for microfluidic applications. The purpose of this chapter is to gain a better understanding of the theory by exploring analytically some of its predictions for channels of different geometry. As the Darcy approximation is usually sufficient for modelling most problems, it will be explored first by constructing one dimensional models for fluid flow in rectangular channels and triangular wedges. Specifically, the effect that different fluidic loads will have on the overall flow rate is examined. Next, a simple one-dimensional model is constructed for flow at the intersection of two channels. These one-dimensional models are compared with numerical results to test their validity. Such models will be useful for obtaining simple, order of magnitude estimates of flow velocities in different device configurations, which would greatly facilitate the design of microfluidic circuits.

The Brinkman approximation will then be used to investigate flow profiles near solid boundaries if the zeta potential of the boundary and the porous material are not equal. Such mismatches will probably be common in microfluidic devices, as different materials will typically have different zeta potentials. An understanding of the thin boundary layer that develops near the solid boundary will be critical in any numerical model that attempts to account for such effects, as the required mesh density near the boundary must be known. The velocity profiles for the case of uncharged walls are examined for flow between two parallel plates, in a cylinder, and in a rectangular channel. A time-dependent version of the Brinkman equation is solved in order to obtain an estimate of the time required for flow to reach steady state.

Finally, the Brinkman equation will be used to model two different wall effects that are commonly seen in capillary electrochromatography (CEC). First, the effect of a zeta potential mismatch between the column wall and the packing material will be considered, and second, the combined effect of increased porosity and increased zeta potential at the column wall will be considered. This is the first time that both effects have been considered together. These models demonstrate the importance of taking into consideration viscous effects near boundaries in certain applications, such as in CEC, as it is seen that the viscous effects near the boundaries have a significant impact on the velocity profile and total volume flow in the capillary. These models will be extended in the next chapter to account for nonlinear effects from high zeta potentials and an oscillating porosity near the boundary wall, and used to fit experimental data from the literature.

4.1 The Darcy approximation

As seen in section 3.2, the Darcy approximation is valid when the Darcy number, D_a , and the fluid velocity are very small. The model for electroosmotic flow in porous media then reduces to

$$\bar{u} = \frac{K}{\sqrt{\tau}\mu_e}(\nabla P + \rho_{eff}\nabla\phi) \quad (4.1)$$

$$\nabla \cdot \bar{u} = 0. \quad (4.2)$$

This one-dimensional model can be used to estimate the volume flow in straight channels, or even in intersecting channels far from the intersection. This will be demonstrated below.

4.1.1 Load modelling

One potentially interesting situation arises when an electric field is applied over only a portion of a channel. Electroosmotic flow will be generated only in this portion, which will be referred to here as an electroosmotic pump. Due to conservation of

mass, the fluid in the upstream or downstream sections must also flow, and thus these sections, combined, act as a load on the pump. If such a configuration was used with open (rather than porous) channels, the backpressure caused by the load would seriously limit the effectiveness of the pump. In the electroosmotic pump region, the velocity profile would no longer be flat, as predicted by Smoluchowski's result 2.71, but instead would have a parabolic velocity profile, due to the backpressure caused by the load. However, if a porous region is used as the electroosmotic pump, the backpressure caused by the extra fluidic resistance of an open channel will be negligible (see Figure 4.1). If the load region is also porous, the backpressure caused by the load will become significant; however, the velocity profile in the porous segments will remain flat. A few simple models that can be used to describe electroosmotic pumps and loads will be developed in this section. For simplicity, the effects of a streaming potential in the load region have been neglected. For porous loads with small pore sizes, streaming potential effects may become significant (see Section 2.2.3).

Initially, it will be assumed that the cross-sectional area and material parameters are identical in both regions. One design issue in such a setup is the length of the load region relative to the length of the pump.

First, assume that the electrodes are placed at each end of the channel of length L so that the entire region acts as an electroosmotic pump. The volume flow, assuming that the applied pressure gradient is zero, will be given by

$$U = \frac{AK}{\sqrt{\tau}\mu_e} \left(\rho_{eff} \frac{\Delta\phi}{L} \right) = \frac{AK}{\sqrt{\tau}\eta_e\rho_w} \left(\rho_{eff} \frac{\Delta\phi}{L} \right). \quad (4.3)$$

Here, it is assumed that the voltage difference, $\Delta\phi$, is applied across the entire channel length. Now, if the electrodes are moved so that they are a distance $(L_2 - L_1)$ apart, where $(L_2 - L_1 \leq L)$, the electric field gradient in the region of the pump is now given by

$$E_{pump} = \frac{\Delta\phi}{L_2 - L_1} = \frac{\Delta\phi}{L} \frac{L}{L_2 - L_1}. \quad (4.4)$$

In order to model the effect of the load region (the region outside the electrodes), it will now be assumed that all the mass in the load region is moved into the region

Figure 4.1: Flow profiles due to backpressure effects in open and porous electroosmotic pumps. (a, c) If electroosmosis is used in an open channel to pump fluid through another of equal length, the backpressure of the load can significantly reduce the flow rate. The radius of both the pump and load is $25 \mu\text{m}$. (b, d) If electroosmosis is used instead in a porous channel to pump fluid through an open channel of equal length, the backpressure of the load will have a very small (often negligible) effect on the flow rate. The radius of both the porous pump and load is $25 \mu\text{m}$. The flow profile is shown inside a single pore inside the pump, with a radius of approximately 225 nm . The flow profiles have been generated using the theory from Sections 2.2.2 and 4.1.

between the electrodes (the electroosmotic pump), increasing its density to a new density, ρ_{pump} . This can be expressed as

$$mass = \rho_w AL = \rho_{\text{pump}} A(L_2 - L_1). \quad (4.5)$$

The new pump density can then be modelled as

$$\rho_{pump} = \rho_w \frac{L}{(L_2 - L_1)}. \quad (4.6)$$

Thus, the volume flow can be expressed as

$$\begin{aligned} U &= \frac{AK}{\sqrt{\tau}\eta_e\rho_{pump}} \left(\rho_{eff} \frac{\Delta\phi}{L} \frac{L}{L_2 - L_1} \right) \\ &= \frac{AK}{\sqrt{\tau}\eta_e\rho_w} \frac{L_2 - L_1}{L} \left(\rho_{eff} \frac{\Delta\phi}{L} \frac{L}{L_2 - L_1} \right) \\ &= \frac{AK}{\sqrt{\tau}\eta_e\rho_w} \left(\rho_{eff} \frac{\Delta\phi}{L} \right), \end{aligned} \quad (4.7)$$

which is the same as equation 4.3 for the case where the electrodes span the entire channel length. Therefore, the increase in the electric field strength balances the effective increase in density, and the load region in this case can be treated as if the electrodes were actually separated by the entire channel length. Thus, the pumping power of the pump is determined by the length of the pump and load regions combined. Note that this will not be true if the channel geometry or material parameters are different in the two different regions. The same principles would apply, but the increase in effective density would have to account for the changing cross-sectional area and material parameters along the channel length.

4.1.2 Kirchhoff's Laws and Fluidic Resistance

More generally, it is possible to model microfluidic circuits by assigning a fluidic resistance to each region. Due to the conservation of mass, Kirchhoff's Current and Voltage Laws can be used to calculate the fluid flow in each element. However, the pressure would take the place of the voltage, the fluid volume flow would take the place of the current, and the fluidic resistance would take the place of the electrical resistance. The analogous form of Ohm's Law for fluid flow would then be

$$\Delta P = UR. \quad (4.8)$$

Assigning the n_{th} region a fluidic resistance R_n , where

$$R_n = \frac{\mu_n \sqrt{\tau_n} L_n}{A_n K_n}, \quad (4.9)$$

and assuming the pump and the loads are in series, Darcy's Law shows that the volume flow can be given by

$$U = \frac{\rho_{eff} \Delta \phi + \Delta P}{R_1 + R_2 + \dots + R_n}. \quad (4.10)$$

If the effective charge density changes from region to region, superposition can be used to sum the individual contributions due to each region, assuming all other regions in the pump are part of the load. However, in order to take into account changes in the electric field density due to changes in the width of the channel, it must be noted that the electrical resistance of a material, R_e is given by

$$R_e = R_s \frac{L}{A}, \quad (4.11)$$

where R_s is the resistivity of the material in question (the fluid and porous medium, in this case). The volume flow can then be given by

$$U = \rho_{eff_{mean}} \left(\frac{\Delta \phi}{R_1 + R_2 + \dots + R_n} \right) + \frac{\Delta P}{R_1 + R_2 + \dots + R_n}, \quad (4.12)$$

where $\rho_{eff_{mean}}$ can be calculated using superposition and voltage division to be

$$\rho_{eff_{mean}} = \frac{\rho_{eff_1} \frac{L_1}{A_1} + \rho_{eff_2} \frac{L_2}{A_2} + \dots + \rho_{eff_p} \frac{L_p}{A_p}}{\frac{L_1}{A_1} + \frac{L_2}{A_2} + \dots + \frac{L_p}{A_p}}, \quad (4.13)$$

where the subscript p represents the p_{th} region of the pump. The above equations have been found to be quite accurate (usually within 1 or 2 percent relative to the numerical models) provided that the cross-sectional area, A , remains constant. Sudden changes in the cross-sectional area reduce the accuracy of the above models due to changes in the velocity profile and the distribution of the applied electric field. This will be demonstrated below.

Variable	Value	Variable	Value	Variable	Value
a_1	50 nm	a_2	600 nm	a_3	1000 nm
ϵ_1	0.8	ϵ_2	0.4	ϵ_3	0.7
ψ_{o1}	60 mV	ψ_{o2}	20 mV	ψ_{o3}	0 mV
W_1	50 μm	W_2	50 μm	W_3	50 μm
L_1	50 μm	L_2	100 μm	L_3	500 μm
ϵ_w	40 ϵ_o	τ	2	η	$5 \times 10^{-7} m^2/s$
$\Delta\phi$	40 V	ρ_w	1000 kg		
$\bar{u}_{Darcy}$	3.052 mm/s	$\bar{u}_{FEM}$	3.052 mm/s	% Δ	0.003 %

Table 4.1: Results for the geometry shown in Figure 4.2. Here, $\bar{u}_{Darcy}$ refers to the volume-averaged flow predicted by the one-dimensional analytical Darcy model, while $\bar{u}_{FEM}$ refers to the numerical results obtained with Femlab. The subscripts for the different variables indicate the porous region for which they were used. The % difference (% Δ) was calculated as (left column – right column)/left column $\times$ 100%.

Figure 4.2: Geometry used in the simulation of a channel of uniform width with three different porosities. See Table 4.1 for the results.

In order to test these models, the complete generalized porous medium equation (3.13) was implemented in Femlab, a commercial software package developed by COMSOL, Inc., and solved for a number of different geometries. Note that double layer effects were neglected in order to simplify the model; incorporating double layer effects into the model was not considered necessary to draw comparisons between the theoretical and numerical models. The first geometry analyzed was a channel of constant width with three regions of different porosity, with the first two regions included in the pump, and the last region included in the load. This is illustrated in Figure 4.2. A comparison of the theoretical and the numerical results is given in Table 4.1. It can be seen that there is excellent agreement between the numerical model and the Darcy approximation.

Variable	Value	Variable	Value	Variable	Value
a_1	50 nm	a_2	600 nm	a_3	1000 nm
ϵ_1	0.8	ϵ_2	0.4	ϵ_3	0.7
ψ_{o1}	60 mV	ψ_{o2}	20 mV	ψ_{o3}	0 mV
W_1	50 μm	W_2	50 μm	W_3	20 μm
L_1	50 μm	L_2	100 μm	L_3	500 μm
ϵ_w	40 ϵ_o	τ	2	η	$5 \times 10^{-7} m^2/s$
$\Delta\phi$	40 V	ρ_w	1000 kg		
$\bar{u}_{Darcy_1}$	2.934 mm/s	$\bar{u}_{FEM_{center1}}$	2.916 mm/s	% Δ	0.603 %
$\bar{u}_{Darcy_2}$	2.934 mm/s	$\bar{u}_{FEM_{center2}}$	2.913 mm/s	% Δ	0.706 %
$\bar{u}_{Darcy_3}$	7.334 mm/s	$\bar{u}_{FEM_{center3}}$	7.455 mm/s	% Δ	-1.630 %
U_{Darcy}	$1.467 \times 10^{-7} m^2/s$	$U_{FEM_{inlet}}$	$1.423 \times 10^{-7} m^2/s$	% Δ	3.064 %
U_{Darcy}	$1.467 \times 10^{-7} m^2/s$	$U_{FEM_{outlet}}$	$1.419 \times 10^{-7} m^2/s$	% Δ	3.347 %
$U_{FEM_{inlet}}$	$1.423 \times 10^{-7} m^2/s$	$U_{FEM_{outlet}}$	$1.419 \times 10^{-7} m^2/s$	% Δ	0.275 %

Table 4.2: Results for the geometry shown in Figure 4.3. Here, $\bar{u}_{Darcy}$ and U_{Darcy} refer to the volume-averaged flow and volume flow predicted by the one-dimensional analytical Darcy model respectively, and $\bar{u}_{FEM_{center}}$ refers to the numerical volume-averaged flow obtained in the center of each channel using Femlab. The numerical subscripts for the different variables indicate the porous region for which they were used. $U_{FEM_{inlet}}$ and $U_{FEM_{outlet}}$ refer to the two-dimensional volume flow for the inlet (left) and outlet (right), respectively, calculated by Femlab. The volume flows calculated by the analytical Darcy model are identical for the inlet and outlet. The % difference (% Δ) was calculated as (left column – right column)/left column $\times$ 100%.

Figure 4.3: Geometry used in the simulation of a channel with a pump of uniform width and two porosities and a load with a different width and different porosity. See Table 4.2 for the results.

The second geometry analyzed was a channel with a pump consisting of two regions of different porosity but identical width, and a load of different width and porosity, as shown in Figure 4.3. The results are given in Table 4.2. Once again, excellent agreement between the numerical model and the Darcy approximation is observed. Both the average flow velocity, $\bar{u}$, and the volume flow, U , are compared with the numerical results. The flow velocity values for the numerical results, $\bar{u}_{FEM_{center}}$, were

taken from the center of each region of the channel. There is a slight increase in the difference between the numerical and theoretical results for the volume flow, U . This is due largely to the no-slip condition, $u = 0$, enforced at the walls of the channel in the numerical model, where the velocity can be expected to decrease rapidly to zero in a thin boundary layer. The mesh used for this particular simulation was not likely dense enough (due to memory constraints) to accurately capture this boundary layer. An estimation of the error in the numerical analysis is also provided by calculating the difference between the inlet and outlet volume flows.

Variable	Value	Variable	Value	Variable	Value
a_1	50 nm	a_2	600 nm	a_3	1000 nm
ϵ_1	0.8	ϵ_2	0.4	ϵ_3	0.7
ψ_{o1}	60 mV	ψ_{o2}	20 mV	ψ_{o3}	0 mV
W_1	20 μm	W_2	50 μm	W_3	50 μm
L_1	50 μm	L_2	100 μm	L_3	500 μm
ϵ_w	40 ϵ_o	τ	2	η	$5 \times 10^{-7} m^2/s$
$\Delta\phi$	40 V	ρ_w	1000 kg		
$\bar{u}_{Darcy_1}$	5.241 mm/s	$\bar{u}_{FEM_{center1}}$	4.828 mm/s	% Δ	8.697 %
$\bar{u}_{Darcy_2}$	2.096 mm/s	$\bar{u}_{FEM_{center2}}$	1.914 mm/s	% Δ	9.553 %
$\bar{u}_{Darcy_3}$	2.096 mm/s	$\bar{u}_{FEM_{center3}}$	1.903 mm/s	% Δ	10.188 %
U_{Darcy}	$1.048 \times 10^{-7} m^2/s$	$U_{FEM_{inlet}}$	$0.889 \times 10^{-7} m^2/s$	% Δ	17.908 %
U_{Darcy}	$1.048 \times 10^{-7} m^2/s$	$U_{FEM_{outlet}}$	$0.926 \times 10^{-7} m^2/s$	% Δ	13.233 %
$U_{FEM_{inlet}}$	$0.889 \times 10^{-7} m^2/s$	$U_{FEM_{outlet}}$	$0.926 \times 10^{-7} m^2/s$	% Δ	-3.965 %

Table 4.3: Results for the geometry shown in Figure 4.4. Here, $\bar{u}_{Darcy}$ and U_{Darcy} refer to the volume-averaged flow and volume flow predicted by the one-dimensional analytical Darcy model respectively, and $\bar{u}_{FEM_{center}}$ refers to the numerical volume-averaged flow obtained in the center of each channel using Femlab. The numerical subscripts for the different variables indicate the porous region for which they were used. $U_{FEM_{inlet}}$ and $U_{FEM_{outlet}}$ refer to the two-dimensional volume flow for the inlet (left) and outlet (right), respectively, calculated by Femlab. The volume flows calculated by the analytical Darcy model are identical for the inlet and outlet. The % difference (% Δ) was calculated as (left column – right column)/left column $\times$ 100%.

The third geometry analyzed was a channel with a pump containing two regions of different widths and porosities, and a load region of different porosity, as seen in Figure 4.4. The results are shown in Table 4.3. A much larger difference between the numerical and Darcy models is observed in this case. This is largely due to the approximation in equation 4.13 for the mean effective charge density. Indeed, if the applied voltage, $\Delta\phi$, is applied only across L_1 , the difference is reduced to a level similar to that seen in the second geometry (Figure 4.3). This suggests that

Figure 4.4: Geometry used in the simulation of a channel with a pump with different widths and porosities and a load with uniform width and porosity. See Table 4.3 for the results.

numerical modelling will be necessary in cases where the pump has sudden changes in cross-sectional area.

4.1.3 The Effective Backpressure of a Load

One could alternatively model the load as an effective backpressure, P_b , working against the pump. The effective backpressure of the load region can be found by setting the total volume flow equal to the flow that would result due to an applied backpressure using the pump alone:

$$U = \frac{\rho_{eff}\Delta\phi + \Delta P}{R_{pump} + R_{load}} = \frac{\rho_{eff}\Delta\phi + \Delta P + P_b}{R_{pump}}. \quad (4.14)$$

Solving for the effective backpressure P_b yields

$$P_b = -\frac{(\rho_{eff}\Delta\phi + \Delta P)R_{load}}{R_{pump} + R_{load}}. \quad (4.15)$$

A theoretical plot of an electroosmotic pump working against an applied backpressure without a load is shown in Figure 4.5 for different voltages. Also shown is a plot of the effective backpressure of a load at different applied voltages. It can be seen that the effective backpressure of the load intersects the load-free lines. The intersection points yield the effective backpressure of the load. This type of plot can be reproduced

in the laboratory, allowing researchers to characterize a particular pump by applying different backpressures and different loads to the pump.

Variable	Symbol	Value	Variable	Symbol	Value
porosity	ϵ	0.7	permittivity	ϵ_w	$45 \epsilon_o$
tortuosity	τ	2	inverse debye length	κ	$1/5nm$
zeta potential	ψ_o	$-20 mV$	coeff of viscosity	μ	$5 \times 10^{-4} Pa s$
width of channel	W	$100 \mu m$	height of channel	H	$50 \mu m$
length of pump	L_1	$1000 \mu m$	length of load	L_2	$200 \mu m$
pore radius	a	$0.1 \mu m$			

Table 4.4: Variables used in the effective backpressure calculations for Figure 4.5

Figure 4.5: Flow rates vs applied backpressure or load. The intersection of the load line with the load-free lines yields the effective backpressure of the load. The values used for the model are given in Table 4.4.

4.1.4 Channels of Non-rectangular Geometry

In some circumstances, it is of interest to design flow channels that are not rectangular. One example of this would be in a wedge-shaped pump, in which the fluid velocity increases as one approaches the narrower end of the pump, channelling the analytes in the fluid together [20].

Figure 4.6: Geometry of a wedge-shaped pump. The pump is symmetric about $y = 0$.

Variable	Value	Variable	Value	Variable	Value
a_1	100 nm	ϵ_1	0.7	ψ_{o1}	-40 mV
L	700 μm	y_1	300 μm	y_2	100 μm
ϵ_w	40 ϵ_o	η	$5 \times 10^{-7} m^2/s$	τ	2
$\Delta\phi$	40 V	ρ_w	1000 kg		
U_{Darcy}	$1.033 \times 10^{-7} m^2/s$	$U_{FEM_{inlet}}$	$1.007 \times 10^{-7} m^2/s$	% Δ	2.603 %
U_{Darcy}	$1.033 \times 10^{-7} m^2/s$	$U_{FEM_{outlet}}$	$1.000 \times 10^{-7} m^2/s$	% Δ	3.269 %
$U_{FEM_{inlet}}$	$1.007 \times 10^{-7} m^2/s$	$U_{FEM_{outlet}}$	$1.000 \times 10^{-7} m^2/s$	% Δ	0.65 %

Table 4.5: Results for the geometry shown in Figure 4.6. Here, U_{Darcy} refers to the volume flow predicted by the one-dimensional analytical Darcy model. $U_{FEM_{inlet}}$ and $U_{FEM_{outlet}}$ refer to the two-dimensional volume flow for the inlet (left) and outlet (right), respectively, calculated by Femlab. The volume flows calculated by the analytical Darcy model are identical for the inlet and outlet. The % difference (% Δ) was calculated as (left column – right column)/left column $\times$ 100%.

The resistance of a channel of arbitrary geometry (assumed to be directed horizontally) can be found by

$$R = \frac{\mu\sqrt{\tau}}{K} \int_0^L \frac{1}{A(x)} dx, \quad (4.16)$$

where $A(x)$ is a function describing the cross-sectional area of the channel over a horizontal length L . For a wedge-shaped pump symmetric about $y = 0$ with initial height y_1 and final height y_2 , as shown in Figure 4.6, the fluidic resistance can be found by

$$R = \frac{1}{2} \frac{\mu\sqrt{\tau}}{K} \int_0^L \frac{1}{mx + y_1} dx = \frac{\mu\sqrt{\tau}}{2mK} \ln \left(\frac{y_2}{y_1} \right), \quad (4.17)$$

where m is the slope, given by $\left(\frac{y_2 - y_1}{L}\right)$. If the electrodes are not placed at the inlet and outlet of the pump, but are placed as shown in Figure 4.7, the total resistance will be given by the sum of the two individual regions:

$$R = R_1 + R_2 = \frac{1}{2} \frac{\mu \sqrt{\tau_1}}{m_1 K_1} \ln \left(\frac{y_2}{y_1} \right) + \frac{1}{2} \frac{\mu \sqrt{\tau_2}}{m_2 K_2} \ln \left(\frac{m_2 L_2 + y_1}{m_2 L_1 + y_1} \right), \quad (4.18)$$

where $m_1 = \left(\frac{y_2 - y_1}{L_1}\right)$ and $m_2 = \left(\frac{y_3 - y_2}{L_2 - L_1}\right)$. These resistances can be plugged back into equation 4.10 to find the volume flow through the pump.

Figure 4.7: Geometry of a wedge-shaped pump followed by a wedge-shaped load. The length L_2 is the total length of the wedge. The pump and load are symmetric about $y = 0$.

The accuracy of this model has been tested by comparing the theoretical result due to Darcy's Law with the solution to the complete generalized porous medium equation for two different electrode configurations for a wedge-shaped pump. The first configuration is that of Figure 4.6. The results of the simulation are given in Table 4.5. It can be seen that the models show satisfactory agreement.

The second configuration is that of Figure 4.7, with a pump and a load contained in the wedge-shaped channel. The results are given in Table 4.6. The Darcy model is seen to be within a few percent of the numerical model.

The geometry of the wedge can be used to control the fluid velocity at the outlet. In

Figure 4.8: Normalized exit velocity of a wedge-shaped pump for different y_3/y_1 and L_1/L_2 ratios. In the left figure, the total length of the wedge L_2 and the distance between the electrodes L_1 are held constant, while the slope is varied using y_1 (the half-width at the inlet) and y_2 (the half-width at the second electrode). In the right figure, the total length of the wedge and the slope are held constant, but the distance between the electrodes, L_1 , is varied. The velocities are normalized with respect to the maximum velocity in each figure.

Figure 4.9: Wedge outlet width (4.9(a)) and the exit velocity of a wedge-shaped pump (4.9(b)), where both L_1 and L_2 are varied. The parameters used were $M = 85nm$, $\sigma_a = 20nm$, $a_{max} = 110nm$, $\mu = 7.48 \times 10^{-7}$ kg/ms, $\kappa = 1/5nm$, $\epsilon = 0.75$, $\tau = 1.4$, $\epsilon_w = 51\epsilon_o$, $\psi_o = -25mV$, $\Delta\phi = 40V$, $y_1 = 4mm$, and $y_2 = 3mm$.

Variable	Value	Variable	Value	Variable	Value
a_1	100 nm	ϵ_1	0.7	ψ_o	-40 mV
a_2	100 nm	ϵ_2	0.4		
L_1	350 μm	y_1	300 μm	y_2	200 μm
L_2	350 μm	y_3	100 μm		
ϵ_w	40 ϵ_o	η	$5 \times 10^{-7} m^2/s$	τ	2
$\Delta\phi$	40 V	ρ_w	1000 kg		
U_{Darcy}	$0.701 \times 10^{-7} m^2/s$	$U_{FEM_{inlet}}$	$0.676 \times 10^{-7} m^2/s$	% Δ	3.759 %
U_{Darcy}	$0.701 \times 10^{-7} m^2/s$	$U_{FEM_{outlet}}$	$0.658 \times 10^{-7} m^2/s$	% Δ	6.582 %
$U_{FEM_{inlet}}$	$0.676 \times 10^{-7} m^2/s$	$U_{FEM_{outlet}}$	$0.658 \times 10^{-7} m^2/s$	% Δ	2.721 %

Table 4.6: Results for the geometry shown in Figure 4.7. Here, U_{Darcy} refers to the volume flow predicted by the one-dimensional analytical Darcy model. $U_{FEM_{inlet}}$ and $U_{FEM_{outlet}}$ refer to the two-dimensional volume flow for the inlet (left) and outlet (right), respectively, calculated by Femlab. The variables ϵ_1 and ϵ_2 refer to the porosity in the pump and load regions, respectively. The volume flows calculated by the analytical Darcy model are identical for the inlet and outlet. The % difference (% Δ) was calculated as (left column – right column)/left column $\times$ 100%.

general, increasing the slope of the walls of the pump (shrinking the outlet width) will increase the fluid velocity at the outlet, as will increasing the ratio of the distance between the electrodes, L_1 , to the total length of the wedge, L_2 . This is illustrated in Figure 4.8. In Figure 4.8(a), the total length of the wedge L_2 and the distance between the electrodes L_1 are held constant, while the slope is varied using y_1 (the half-width at the inlet) and y_2 (the half-width at the second electrode). In Figure 4.8(b), the total length of the wedge and the slope is held constant, but the distance between the electrodes, L_1 , is varied.

These effects will compete with each other if L_1 and L_2 are varied simultaneously, as the slope will depend on the total length of the wedge L_2 . This is illustrated in Figure 4.9. It has been assumed that the wedge is made from a heterogeneous porous material with an average pore size M of 85 nm, a standard deviation σ_a of 20 nm, and a maximum pore radius a_{max} of 110 nm, and thus the permeability K will be slightly different in the pump and load regions. The viscosity μ was 7.48×10^{-7} kg/ms, the inverse Debye length κ was 1/5nm, the porosity ϵ was 0.75, the tortuosity τ was 1.4, the permittivity was $\epsilon_w = 51\epsilon_o$, the zeta potential ψ_o was -25 mV, and the applied potential was 40 V. The inlet half-width y_1 was 4 mm, and the half-width at the electrodes y_2 was 3 mm. The width of the outlet can be seen to be the dominating factor; the highest velocity in this case is achieved with a total length L_2 of 7 mm

and a distance between the electrodes L_1 of only 2 mm, as, for this case, the outlet half-width is only 0.5 mm.

4.1.5 Intersection Modelling using Darcy's Law

Microfluidic circuits invariably require interconnecting channels to direct fluids from one region of the chip to another. If the appropriate voltages are applied at each end of the intersecting channels, the fluid flow can be shunted in the desired direction. However, there is usually still some leakage in other directions. If the channels are porous, Darcy's Law can be used to estimate the amount of fluid flow in each arm of the intersecting channels. Note that the velocity estimates will only be valid far from the intersection itself.

Figure 4.10: Geometry for the two channel intersection modelled in Table 4.7.

Each channel can be treated as a resistive element in a fluidic circuit, and Kirchhoff's Laws can be used to determine the net flow from a given node. If the voltage and pressure at the center node are ϕ_x and P_x , respectively, and ϕ_1 , ϕ_2 , ϕ_3 , and ϕ_4 are the voltages at the top, bottom, left, and right arms, respectively, at distances L_1 , L_2 , L_3 , and L_4 from the center node, the volume flow in each arm can be found by

$$U_n = \frac{P_x + (\phi_x - \phi_n)\rho_{effn}}{R_n}. \quad (4.19)$$

Figure 4.11: Flow lines at the intersection for the geometry shown in Figure 4.10. The values used in the simulation are given in Table 4.7. The size of the arrows has been scaled to reflect the magnitude of the velocity at a given location.

The center node voltage ϕ_x can be determined by solving

$$\frac{(\phi_1 - \phi_x)}{\frac{L_1}{A_1}} + \frac{(\phi_2 - \phi_x)}{\frac{L_2}{A_2}} + \frac{(\phi_3 - \phi_x)}{\frac{L_3}{A_3}} + \frac{(\phi_4 - \phi_x)}{\frac{L_4}{A_4}} = 0, \quad (4.20)$$

to which the solution is

$$\phi_x = \frac{\frac{A_1\phi_1}{L_1} + \frac{A_2\phi_2}{L_2} + \frac{A_3\phi_3}{L_3} + \frac{A_4\phi_4}{L_4}}{\frac{A_1}{L_1} + \frac{A_2}{L_2} + \frac{A_3}{L_3} + \frac{A_4}{L_4}}. \quad (4.21)$$

The pressure at the center node, P_x , arises due to conservation of mass. It can be found by solving

$$\sum_{i=1}^n U_n = 0, \quad (4.22)$$

to which the solution is

$$P_x = - \frac{\frac{\rho_{eff1}(\phi_x - \phi_1)}{R_1} + \frac{\rho_{eff2}(\phi_x - \phi_2)}{R_2} + \frac{\rho_{eff3}(\phi_x - \phi_3)}{R_3} + \frac{\rho_{eff4}(\phi_x - \phi_4)}{R_4}}{\frac{1}{R_1} + \frac{1}{R_2} + \frac{1}{R_3} + \frac{1}{R_4}}. \quad (4.23)$$

Variable	Value	Variable	Value	Variable	Value
a_1	50 nm	ϵ_1	0.8	ψ_{o_1}	60 mV
a_2	600 nm	ϵ_2	0.4	ψ_{o_2}	20 mV
a_3	1 μm	ϵ_3	0.7	ψ_{o_3}	30 mV
a_4	2 μm	ϵ_4	0.5	ψ_{o_4}	50 mV
L_1	280 μm	A_1	50 μm	ϕ_1	40 V
L_2	525 μm	A_2	40 μm	ϕ_2	20 V
L_3	375 μm	A_3	40 μm	ϕ_3	-10 V
L_4	320 μm	A_4	50 μm	ϕ_4	0 V
ϵ_w	40 ϵ_o	η	$5 \times 10^{-7} m^2/s$	τ	2
ρ_w	1000 kg				
$\bar{u}_{Darcy_1}$	1.088 mm/s	$\bar{u}_{FEM_{center1}}$	1.112 mm/s	% Δ	-2.1 %
$\bar{u}_{Darcy_2}$	1.748 $\mu m/s$	$\bar{u}_{FEM_{center2}}$	19.451 $\mu m/s$	% Δ	-91.0 %
$\bar{u}_{Darcy_3}$	0.473 mm/s	$\bar{u}_{FEM_{center3}}$	0.527 mm/s	% Δ	-10.2 %
$\bar{u}_{Darcy_4}$	0.711 mm/s	$\bar{u}_{FEM_{center4}}$	0.715 mm/s	% Δ	-0.6 %
U_{Darcy_1}	$0.544 \times 10^{-7} m^2/s$	U_{FEM_1}	$0.533 \times 10^{-7} m^2/s$	% Δ	2.1 %
U_{Darcy_2}	$0.699 \times 10^{-10} m^2/s$	U_{FEM_2}	$7.378 \times 10^{-10} m^2/s$	% Δ	-90.5 %
U_{Darcy_3}	$0.189 \times 10^{-7} m^2/s$	U_{FEM_3}	$0.200 \times 10^{-7} m^2/s$	% Δ	-5.6 %
U_{Darcy_4}	$0.355 \times 10^{-7} m^2/s$	U_{FEM_4}	$0.345 \times 10^{-7} m^2/s$	% Δ	2.9 %
$(U_1 + U_2) - (U_3 + U_4)$	$-8.7 \times 10^{-14} m^2/s$ (Darcy)	$(U_1 + U_2) - (U_3 + U_4)$	$-5.312 \times 10^{-10} m^2/s$ (FEM)	% Δ	-99.9 %

Table 4.7: Results for the intersection shown in Figure 4.10. Here, $\bar{u}_{Darcy}$ and U_{Darcy} refer to the volume-averaged flow and volume flow predicted by the one-dimensional analytical Darcy model respectively, and $\bar{u}_{FEM_{center}}$ refers to the numerical volume-averaged flow obtained in the center of each channel using Femlab. The numerical subscripts for the different variables indicate the porous region for which they were used. $U_{FEM_{inlet}}$ and $U_{FEM_{outlet}}$ refer to the two-dimensional volume flow for the inlet (left) and outlet (right), respectively, calculated by Femlab. The % difference (% Δ) was calculated as (left column – right column)/left column $\times$ 100%. The error in the numerical model can be estimated by testing how well conservation of mass has been maintained using $(U_1 + U_2) - (U_3 + U_4)$. It can be seen that the numerical model has difficulty resolving the low flow velocities in the second arm of the intersection.

These models have been evaluated by comparing their predictions with the Femlab solution to the complete generalized porous medium equation in two intersecting channels. The geometry used is shown in Figure 4.10, and the results are shown in Table 4.7. Each arm of the cross had different material properties, and a different potential was applied at each channel. A mesh of 6500 elements was used. From the results, it is apparent that the velocity in the second arm is very small; the flow in the first arm is due almost entirely to the combination of the third and fourth arms. This shows that the flow can be shunted in a desired direction by selecting the appropriate voltage at each arm, with only a small leakage flow (three orders of magnitude smaller). The Darcy model and the numerical model show good agreement for most of the results, with the exception of the second arm, where larger

error can be expected due to the relatively low velocity in this arm. Comparing the sum of the volume flow from the inlet and outlet arms, which should ideally be zero ($U_1 + U_2 - U_3 - U_4 = 0$), suggests that the numerical model is unable to accurately calculate the flow in the second arm. The flow lines at the intersection from the numerical model are illustrated in Figure 4.11, showing how the fluid behaves near the intersection. This information could not be easily obtained from a one-dimensional Darcy model.

Figure 4.12: Flow lines at the intersection using the geometry shown in Figure 4.10, but with rounded corners. The values used in the simulation are given in Table 4.8.

In an attempt to reduce the error in the numerical model, the mesh density was increased near the corners of the intersection, as it was presumed that the numerical model may be having difficulty resolving the flow in this region. It was found that if the mesh density near the intersection was increased, the difference between the numerical model and the Darcy model did not necessarily improve; in fact, it became worse. However, if the corners at the intersection were made slightly rounded, it was found that increasing the mesh density did improve the error. The results for the case with the rounded corners for the same material parameters as before are presented in Figure 4.12 and Table 4.8. A total of 8700 elements were used, with a minimum element size of $0.5\mu\text{m}$ at the rounded edges. It can be seen that the error does improve with a denser mesh, provided that the corners at the intersection are slightly rounded. If the corners at the intersection were not rounded, effects due to

Variable	Value	Variable	Value	Variable	Value
$\bar{u}_{\text{Darcy}_1}$	1.088 mm/s	$\bar{u}_{\text{FEM}_{\text{center}1}}$	1.123 mm/s	% Δ	-3.2 %
$\bar{u}_{\text{Darcy}_2}$	1.748 $\mu\text{m/s}$	$\bar{u}_{\text{FEM}_{\text{center}2}}$	12.352 $\mu\text{m/s}$	% Δ	-85.8 %
$\bar{u}_{\text{Darcy}_3}$	0.473 mm/s	$\bar{u}_{\text{FEM}_{\text{center}3}}$	0.504 mm/s	% Δ	-6.2 %
$\bar{u}_{\text{Darcy}_4}$	0.711 mm/s	$\bar{u}_{\text{FEM}_{\text{center}4}}$	0.737 mm/s	% Δ	-3.6 %
U_{Darcy_1}	$0.544 \times 10^{-7} \text{ m}^2/\text{s}$	U_{FEM_1}	$0.539 \times 10^{-7} \text{ m}^2/\text{s}$	% Δ	0.9 %
U_{Darcy_2}	$0.699 \times 10^{-10} \text{ m}^2/\text{s}$	U_{FEM_2}	$4.713 \times 10^{-10} \text{ m}^2/\text{s}$	% Δ	-85.2 %
U_{Darcy_3}	$0.189 \times 10^{-7} \text{ m}^2/\text{s}$	U_{FEM_3}	$0.193 \times 10^{-7} \text{ m}^2/\text{s}$	% Δ	-1.8 %
U_{Darcy_4}	$0.355 \times 10^{-7} \text{ m}^2/\text{s}$	U_{FEM_4}	$0.357 \times 10^{-7} \text{ m}^2/\text{s}$	% Δ	-0.3 %
$(U_1 + U_2) - (U_3 + U_4)$ (Darcy)	$-8.7 \times 10^{-14} \text{ m}^2/\text{s}$	$(U_1 + U_2) - (U_3 + U_4)$ (FEM)	$-5.587 \times 10^{-10} \text{ m}^2/\text{s}$	% Δ	-99.9 %

Table 4.8: Results for the intersection shown in Figure 4.12. The material parameters are the same as those used in Table 4.7. $\bar{u}_{\text{Darcy}}$ and U_{Darcy} refer to the volume-averaged flow and volume flow predicted by the one-dimensional analytical Darcy model respectively, and $\bar{u}_{\text{FEM}_{\text{center}}}$ refers to the numerical volume-averaged flow obtained in the center of each channel using Femlab. The numerical subscripts for the different variables indicate the porous region for which they were used. $U_{\text{FEM}_{\text{inlet}}}$ and $U_{\text{FEM}_{\text{outlet}}}$ refer to the two-dimensional volume flow for the inlet (left) and outlet (right), respectively, calculated by Femlab. The % difference (% Δ) was calculated as (left column – right column)/left column $\times$ 100%. The error in the numerical model can be estimated by testing how well conservation of mass has been maintained using $(U_1 + U_2) - (U_3 + U_4)$. It can be seen that the numerical model has difficulty resolving the low flow velocities in the second arm of the intersection.

singularities at the corners become amplified. Memory constraints prevented further increases in mesh density.

4.2 Steady porous electroosmotic flow between two parallel plates

In this section, the electroosmotic velocity profile between two parallel plates in a porous channel will be investigated. It will be assumed that the porous medium is charged, but the walls bounding the medium are uncharged. This model can provide an estimate of the boundary layers that might be seen in porous rectangular channels on a microfluidic chip. It will be assumed that the flow is steady, and slow enough that the nonlinear terms in the generalized porous medium equation (3.13) can be neglected. The resulting equation is a Brinkman equation (3.24):

$$\frac{\eta}{\sqrt{\tau}} \nabla^2 \left(\frac{\bar{u}}{\epsilon} \right) - \frac{\eta_e \bar{u}}{K} = \frac{1}{\sqrt{\tau} \rho_w} (\nabla P + \rho_{eff} \nabla \phi). \quad (4.24)$$

It will be assumed that the applied pressure and electric field, and thus the flow, are parallel to the two plates (i.e. in the $\pm x$ -direction), which are located at $y = \pm b$. The no-slip condition ($u = 0$) will be applied at the channel walls ($y = \pm b$). This geometry is illustrated in Figure 4.13.

Figure 4.13: Geometry used to determine the flow profiles between two parallel plates.

In the following, for convenience, the pressure and electric field terms will be lumped together into a single term, G :

$$G = \nabla P + \rho_{eff} \nabla \phi. \quad (4.25)$$

The flow in this system will then be governed by the following non-homogenous differential equation:

$$\frac{\partial^2 \bar{u}}{\partial y^2} - \frac{\eta_e \epsilon \sqrt{\tau}}{\eta K} \bar{u} = \epsilon \frac{G}{\mu}. \quad (4.26)$$

The solution to the homogeneous case (i.e. with the right-hand side set to zero) is in the form

$$u_h(y) = A \cosh(\lambda y) + B \sinh(\lambda y) \quad (4.27)$$

where λ will be referred to as the inverse *Brinkman screening length* [35], in units of $1/m$, and plays a role very similar to that of the Debye screening length in electroosmotic flow in open channels. In this case, λ is given by

$$\lambda = \sqrt{\frac{\epsilon \sqrt{\tau} \eta_e}{K \eta}}. \quad (4.28)$$

The particular solution to this problem is of the form

$$u_p(y) = Cy^2 + Dy + E. \quad (4.29)$$

Inserting equation 4.29 into equation 4.26 and collecting like terms, the particular solution is

$$u_p = -\frac{GK}{\mu\sqrt{\tau}} \frac{\eta}{\eta_e}. \quad (4.30)$$

Summing the particular and homogenous solutions and applying the boundary conditions $u = 0$ at $y = \pm b$, the solution can be found to be

$$\bar{u}(y) = \frac{(\nabla P + \rho_{eff} \nabla \phi)K}{\mu\sqrt{\tau}} \frac{\eta}{\eta_e} \left(\frac{\cosh(\lambda y)}{\cosh(\lambda b)} - 1 \right). \quad (4.31)$$

Figure 4.14: Flow profiles between two parallel plates for different ratios of the porous channel half-width, b , to the average pore size, a .

The Brinkman screening length λ defines a small boundary layer close to the wall in which the fluid velocity goes to zero very quickly (exponentially). The thickness of the boundary layer is given by $1/\lambda$, and is thus largely determined by the square root of the permeability, K . If the medium is composed of hollow, tortuous cylinders, the permeability can be approximated by $K = \frac{\epsilon a^2}{8\sqrt{\tau}}$ (equation 2.40), and the boundary layer thickness will therefore typically be just a fraction of a single pore's radius. The

ratio λb is the ratio of the channel half-width to the boundary layer thickness. The ratio of hyperbolic cosine terms in equation 4.31 is approximately zero throughout most of the channel when the channel half-width is much larger than the boundary layer ($\lambda b \gg 1$), indicating that the fluid velocity will be constant there. The effects of the boundary layer on the fluid velocity therefore must be considered only when λb is relatively small. In the experimental capillary electrochromatography (CEC) columns investigated in the next chapter, the ratio of the particle diameter to the cylinder diameter is less than 6, and thus boundary layer effects could become important. The flow profiles in a porous channel using the above approximation for the permeability are plotted in Figure 4.14.

The volume flow can be found by integrating over the height of the channel. The result is

$$U = \frac{(\nabla P + \rho_{eff} \nabla \phi) 2bK}{\mu \sqrt{\tau}} \frac{\eta}{\eta_e} \left(\frac{\tanh(\lambda b)}{\lambda b} - 1 \right). \quad (4.32)$$

4.3 Time-dependent porous electroosmotic flow between two parallel plates

The analysis presented so far has only considered steady state flow, i.e. it has been assumed that the flow is already fully-developed. However, the time required for the flow profile to become fully-developed may be of practical importance to microfluidic designers. This section is devoted to finding an estimate of the time constant for the porous medium.

The analysis that follows will neglect processes occurring in the double layer. An analysis of the time-development of the electroosmotic flow profile in the double layer region of an open channel has been given by Soderman and Jonsson [65]. They found that the velocity typically reached its maximum in the double layer in a few nanoseconds, but took much longer to reach its maximum in the rest of the channel, as the only force exerted on the fluid outside the double layer is the viscous force. Equation 27 of Soderman and Jonsson [65] describes the electroosmotic flow profile over time

in an open channel bounded by two parallel plates:

$$\begin{aligned}
 u(y, t) &= \frac{\epsilon_w \psi_o \nabla \phi}{\mu} \left[\left(\frac{\cosh(\kappa y)}{\cosh(\kappa b)} - 1 \right) + \right. \\
 &\quad \left. \sum_{n=0}^{\infty} 2(-1)^n \left(\frac{1}{p} - \frac{\frac{b}{\kappa}}{b^2 + \frac{p^2}{\kappa^2}} \right) \cos\left(\frac{py}{b}\right) e^{-\frac{p^2 \eta t}{b^2}} \right], \\
 p &= \left(n + \frac{1}{2}\right)\pi.
 \end{aligned} \tag{4.33}$$

Figure 4.15: Development of the electroosmotic flow profile between two charged parallel plates in an open medium. The half-width of the channel, b , is 100 nm, while the double layer thickness is 10 nm, or $0.1b$. The time constant is $t_{crit} = 49.35 ns$.

This equation has been plotted for two different channel widths at different times in Figures 4.15 and 4.16. It can be seen that the velocity quickly reaches its maximum inside the double layer. Outside the double layer, the maximum is reached more slowly due to the viscous transfer of momentum.

From equation 4.33, it can be seen that the time constant for electroosmotic flow

Figure 4.16: Development of the electroosmotic flow profile between two charged parallel plates in an open medium. The half-width of the channel, b , is $1 \mu m$, while the double layer thickness is 10 nm , or $0.01b$. The flow has not reached steady-state ($t < t_{crit} = 4.9348 \mu s$) outside the double layer.

development between two parallel plates can therefore be approximated as

$$t_{crit} = \frac{b^2 4}{\eta \pi^2}. \quad (4.34)$$

This can be shown to be identical to the time constant found for pressure-driven flow between two parallel plates. The time constant will vary greatly depending on the width of the channel due to its b^2 dependence. For example, a channel with a half-width of 10 mm and a viscosity of $\eta = 5 \times 10^{-7} \text{ m}^2/\text{s}$ will have a time constant of 81 s , a channel with a half-width of $500 \mu m$ will have a time constant of $500 \mu s$, and a channel with a half-width of 100 nm will have a time constant of approximately 8 ns . This will have significant ramifications on fluid flow in a porous medium; the time constant should be expected to vary according to the radius of the pores, rather than the width of the porous channel. Porous channels can therefore be expected to react much more quickly to the application of a pressure or electric field gradient than open channels.

In order to model the flow profile development in a porous medium, a time-dependent

version of the Brinkman equation must be solved. Although the effective charge density does take into consideration the effects of the double layer on volume flow, the effect of the double layer on the time development of the flow profile is lost in the Brinkman equation, as the charge density profile is required in order to determine the force on the fluid in the double layer region. Thus, the assumption must be made that the double layers are thin relative to the pore radius, so that most of the force on the fluid is carried by viscous drag. If this assumption is not true, it can be expected that the fluid will reach steady state sooner than the following theory predicts. It will be assumed once again that the walls bounding the medium are uncharged.

The time-dependent Brinkman equation for flow between two parallel plates is given by

$$\frac{\sqrt{\tau}}{\epsilon} \frac{\partial \bar{u}}{\partial t} - \frac{\eta}{\sqrt{\tau}\epsilon} \frac{\partial^2 \bar{u}}{\partial y^2} + \eta_e \frac{\bar{u}}{K} = -\frac{(\nabla P + \rho_{eff} \nabla \phi)}{\rho_w \sqrt{\tau}}. \quad (4.35)$$

This is a nonhomogenous partial differential equation. The solution can therefore be given as the sum of the particular solution and the complementary solution. The particular solution will be given by equation 4.31. The complementary solution can be found by solving the left hand side of equation 4.35 (with the right hand side set to zero) using the method of separation of variables. Using the initial condition $u|_{t=0} = 0$ and the boundary conditions $u|_{r=\pm b} = 0$, the final solution is given by

$$\begin{aligned} \bar{u}(y, t) &= \frac{(\nabla P + \rho_{eff} \nabla \phi)K}{\mu \sqrt{\tau}} \frac{\eta}{\eta_e} \left[\left(\frac{\cosh(\lambda y)}{\cosh(\lambda b)} - 1 \right) + \right. \\ &\quad \left. \frac{2}{b} \sum_{n=0}^{\infty} \frac{(-1)^n}{p} \left(1 - \frac{p^2}{R^2} \right) \cos(py) e^{-\frac{R^2 \eta t}{\tau}} \right], \\ p &= \frac{(2n+1)\pi}{2b}, R^2 = p^2 + \lambda^2. \end{aligned} \quad (4.36)$$

This problem has also been solved using the method of variation of parameters, and the two solutions were found to be equivalent. The flow profile development for two different b/a ratios are shown in Figures 4.17, 4.18, and 4.19. The time constant for the development of the the flow profile in a porous medium between two parallel

Figure 4.17: Development of the flow profile over time between two parallel plates in a porous channel with $b = 100\mu m$ and $a = 500nm$.

Figure 4.18: Development of the flow profile over time between two parallel plates in a porous channel with $b = 1\mu m$ and $a = 100nm$.

Figure 4.19: Approach to the maximum flow velocity between two parallel plates in the center of a porous channel with $b = 100\mu m$ and $a = 500nm$.

plates is seen from equation 4.36 to be

$$t_{crit} = \frac{\tau}{R^2\eta}. \quad (4.37)$$

The order of magnitude of the parameter R^2 can be approximated as

$$\begin{aligned} R^2 &= p^2 + \lambda^2 = \left(\frac{(2n+1)\pi}{2b} \right)^2 + \frac{\epsilon\sqrt{\tau}}{K} \frac{\eta_e}{\eta} \\ &= \left(\frac{(2n+1)\pi}{2b} \right)^2 + \frac{8\tau}{a^2} \frac{\eta_e}{\eta} \approx \frac{8\tau}{a^2} \frac{\eta_e}{\eta}, \end{aligned} \quad (4.38)$$

where equation 2.40 for the permeability was used as well as the fact that $a \ll b$. The time constant can then be approximated as

$$t_{crit} = \frac{\tau}{R^2\eta} \approx \frac{a^2}{8\eta_e}. \quad (4.39)$$

The above equation verifies that the time constant of a porous medium is in fact dependent on the radius of the average pore size in the medium, a , rather than the width of the porous channel itself. The time constant will therefore usually be on the

order of a few nanoseconds to a few microseconds (if $a = 5\mu m$ and $\eta = 5 \times 10^{-7} m^2/s$, $t_{crit} \approx 6\mu s$). This implies that, with the exception of applications requiring extremely fast switching times, the flow profile development over time can usually be neglected, and the flow can be assumed to be at steady state. This will be assumed throughout the rest of this work.

4.4 Steady electroosmotic flow in a porous tube

In this section, the velocity profiles at steady state in a porous cylinder of radius b will be considered. Once again, it will be assumed that the flow velocity is small enough that the nonlinear terms in the generalized porous medium equation can be neglected, resulting in a Brinkman equation. It will be assumed as well that the porous medium is charged, but the walls bounding the medium are uncharged. The pressure gradient and electric field are assumed to be applied in the axial (z) direction. Due to symmetry, the r and θ velocity components can be ignored, and only the axial velocity component needs to be considered. The Brinkman equation in cylindrical polar coordinates is therefore given by

$$\frac{\eta}{\sqrt{\tau}\epsilon} \frac{\partial^2 \bar{u}}{\partial r^2} + \frac{\eta}{\sqrt{\tau}\epsilon} \frac{1}{r} \frac{\partial \bar{u}}{\partial r} - \eta_e \frac{\bar{u}}{K} = \frac{(\nabla P + \rho_{eff} \nabla \phi)}{\rho_w \sqrt{\tau}}. \quad (4.40)$$

Multiplying both sides by r^2 and rearranging, it becomes

$$r^2 \frac{\partial^2 \bar{u}}{\partial r^2} + r \frac{\partial \bar{u}}{\partial r} - r^2 \lambda^2 \bar{u} = r^2 \epsilon \frac{(\nabla P + \rho_{eff} \nabla \phi)}{\mu}, \quad (4.41)$$

where λ is given by equation 4.28. This is seen to be a nonhomogenous modified Bessel equation. The complementary solution is therefore given by

$$\bar{u}_c(r) = AI_o(\lambda r) + BK_o(\lambda r). \quad (4.42)$$

Since the fluid velocity must be finite at $r = 0$, we must have $B = 0$. The particular solution will be in the form

$$\bar{u}_p(r) = Cr^2 + Dr + E. \quad (4.43)$$

Plugging this back into the original partial differential equation and collecting like terms results in

$$\bar{u}_p(r) = -\frac{(\nabla P + \rho_{eff}\nabla\phi)K}{\mu\sqrt{\tau}}\frac{\eta}{\eta_e}, \quad (4.44)$$

which can be seen to be equal to Darcy's Law (equation 3.26). Combining the particular and complementary solutions and applying the boundary condition $u = 0$ at the cylinder wall ($r = b$) results in

$$\bar{u}(r) = \frac{(\nabla P + \rho_{eff}\nabla\phi)K}{\mu\sqrt{\tau}}\frac{\eta}{\eta_e} \left(\frac{I_o(\lambda r)}{I_o(\lambda b)} - 1 \right). \quad (4.45)$$

This is analogous to the solution for fluid flow due to electroosmotic flow in a small cylinder in the case of small zeta potentials (see equation 2.76 and Figure 2.6). The boundary layer near the wall in this case, however, is defined by the Brinkman screening length, λ . The volume flow can be found by integrating over the cross-sectional area of the channel, $A = 2\pi b$, and is given by

$$U = \frac{(\nabla P + \rho_{eff}\nabla\phi)AK}{\mu\sqrt{\tau}}\frac{\eta}{\eta_e} \left(\frac{2I_1(\lambda b)}{\lambda b I_o(\lambda b)} - 1 \right). \quad (4.46)$$

This model for electroosmotic flow will not be adequate for flow modelling in some practical applications, such as in capillary electrochromatography (CEC). In CEC, fluid is forced through capillaries packed with small spheres. However, due to the nature of the packing process, the packing becomes less dense near the capillary wall, greatly increasing the porosity in that region. This can result in significantly increased flow near the edges, especially if the fluid is driven by a pressure gradient. For electroosmotically driven flow, it is often the case that the zeta potential at the wall is not equal to the zeta potential on the spheres, once again enhancing fluid flow near the capillary wall. These effects will be considered in later sections.

4.5 Steady electroosmotic flow in a porous rectangular channel

In practice, many microfluidic channels tend to be rectangular in shape. Thus, the effects of a finite width and a finite height must be taken into consideration. Once again making the usual assumptions that the flow velocity is small enough that the nonlinear components of the generalized porous medium equation can be neglected, and that the flow is in the z -direction only, the Brinkman equation in two dimensions in Cartesian coordinates for a rectangle of height $2b$ and width $2a$ is

$$\frac{\partial^2 \bar{u}}{\partial x^2} + \frac{\partial^2 \bar{u}}{\partial y^2} - \lambda^2 \bar{u} = \epsilon \frac{G}{\mu}, \quad (4.47)$$

where λ is given by equation 4.28 and G is given by equation 4.25. This is once again a non-homogenous equation. The particular solution will be given by equation 4.31. The complementary solution will be found by setting the right-hand side of equation 4.47 to zero, and using separation of variables with the no-slip boundary condition on all four walls. Superposition of the two solutions then results in

$$\begin{aligned} \bar{u}(x, y) &= \frac{GK}{\mu\sqrt{\tau}} \frac{\eta}{\eta_e} \left(\frac{\cosh(\lambda y)}{\cosh(\lambda b)} - 1 \right) + \\ &\quad \frac{2}{b} \frac{GK}{\mu\sqrt{\tau}} \frac{\eta}{\eta_e} \sum_{n=0}^{\infty} \frac{(-1)^n}{qb} \frac{\lambda^2}{\lambda^2 + q^2} \left(\frac{\cosh(px)}{\cosh(py)} \right) \cos(qy), \\ p^2 &= \lambda^2 + q^2, q = \frac{(2n+1)\pi}{2b} \end{aligned} \quad (4.48)$$

This is identical to Al-Hadhrami's [66] solution to the Brinkman equation in a rectangular channel. Al-Hadhrami went on to solve the Brinkman equation in rectangular and cylindrical channels with two or three regions of different porosities. The analysis for a rectangular channel with multiple porosities will not be given here.

The volume flow in a rectangular channel can be found by integrating equation 4.48

over the cross-sectional area of the channel. The result is

$$\begin{aligned}
 U &= \frac{AGK}{\mu\sqrt{\tau}} \frac{\eta}{\eta_e} \left(\frac{\tanh(\lambda b)}{\lambda b} - 1 \right) + \\
 &\quad \frac{2AGK}{\mu\sqrt{\tau}} \frac{\eta}{\eta_e} \sum_{n=0}^{\infty} \left(\frac{1}{qb} \right)^2 \frac{\lambda^2}{\lambda^2 + q^2} \left(\frac{\tanh(pa)}{pa} \right), \\
 p^2 &= \lambda^2 + q^2, q = \frac{(2n+1)\pi}{2b},
 \end{aligned} \tag{4.49}$$

where $A = 4ab$ is the cross-sectional area of the channel.

4.6 Accounting for zeta potential mismatches between the walls and the packing material

As mentioned earlier, it is often the case in capillary electrochromatography that the zeta potential of the walls is higher than the potential on the spheres. This section will examine the impact of these mismatches on the flow profile in three steps. First, the case of electroosmotic flow in a porous medium made with an uncharged packing material will be considered. Then, the case of electroosmotic flow in a porous medium with charged walls and a charged packing material will be considered to be the superposition of the cases of flow in a porous medium without charged walls, but a charged packing material, and in a medium with charged walls but an uncharged packing material. A slightly different analysis to the one presented here was given in Rathore and Horvath's work [23] (see Section 2.3); the results will be seen to be quite similar. Finally, the increase in porosity near the wall will then be taken into consideration as well by solving for the flow in a porous channel with two regions of different porosity.

4.6.1 Steady porous flow in an uncharged medium with charged walls

In this section, it will be assumed that electroosmotic flow occurs in a capillary of radius b with charged walls but uncharged packing material. It will be assumed that the wall charge is small enough that the Poisson-Boltzmann equation (2.55) can be

linearized (2.72). Furthermore, changes in permittivity between the particles and the fluid will be neglected. Although a number of different homogenization theories exist that attempt to calculate an effective permittivity in porous media [67,68,69,70], it is unlikely that these models would apply in a region of only a few nanometers thickness (i.e. in the double layer regions). In addition, it must also be remembered that, in practical CEC systems, the porosity approaches a value of unity as the wall is approached, and thus neglecting the effects of the spheres on the permittivity becomes more reasonable.

Effects of porosity variation on the flow profile will also be neglected. It should be noted once again that the electroosmotic flow velocity in a pore is only a function of pore size if the double layer thickness is large relative to the size of the pore (or solid sphere). In most practical CEC systems, the double layer thickness is small (a few nanometers) relative to the radius of the sphere (0.25-20 μm). As a result, an increase in pore size due to the variation in porosity near the wall might be expected to have a minimal impact on the flow profile in electroosmotic flow (this would not be true for pressure-driven flow). However, it will be seen that the increase in velocity due to the mismatch in zeta potentials will be limited to a small region near the wall that is dependent on the permeability, implying the effect of porosity increase near the wall will be significant for electroosmotic flow. Porosity variation will be neglected initially, but taken into consideration later in this section.

Since the wall charge is assumed to be small, the charge density in the capillary can be expressed using equations 2.57, 2.59, and 2.75:

$$\rho = -\frac{2n^o z^2 e^2}{kT} \psi(r) = -\epsilon_w \kappa^2 \psi_{wall} \frac{I_o(\kappa r)}{I_o(\kappa b)}, \quad (4.50)$$

where ψ_{wall} is the zeta potential of the capillary wall. The flow in the capillary will be governed by the following Brinkman equation

$$\frac{\eta}{\sqrt{\tau} \epsilon} \frac{\partial^2 \bar{u}}{\partial r^2} + \frac{\eta}{\sqrt{\tau} \epsilon} \frac{1}{r} \frac{\partial \bar{u}}{\partial r} - \eta_e \frac{\bar{u}}{K} = -\frac{(\epsilon_w \kappa^2 \psi_{wall} \nabla \phi)}{\rho_w \sqrt{\tau}} \frac{I_o(\kappa r)}{I_o(\kappa b)}. \quad (4.51)$$

Rearranging and multiplying by r^2 , one obtains

$$r^2 \frac{\partial^2 \bar{u}}{\partial r^2} + r \frac{\partial \bar{u}}{\partial r} - r^2 \lambda^2 \bar{u} = -H r^2 \frac{I_o(\kappa r)}{I_o(\kappa b)},$$

$$H = \frac{(\epsilon \epsilon_w \kappa^2 \psi_{wall} \nabla \phi)}{\mu}. \quad (4.52)$$

It can be seen that the left hand side is a modified Bessel equation, with a complementary solution identical to that given in equation 4.42. The right hand side suggests a particular solution of the form

$$\bar{u}_p(r) = H \frac{I_o(\kappa r)}{I_o(\kappa b)} (Ar^2 + Br + C). \quad (4.53)$$

Plugging this back into equation 4.51, applying the no-slip boundary condition ($u = 0$) on the walls, and using $\frac{\partial u}{\partial r} = 0$ at the center of the capillary, the particular solution can be expressed as

$$\bar{u}_p(r) = \left(\frac{1}{\lambda^2 - \kappa^2} \right) H \frac{I_o(\kappa r)}{I_o(\kappa b)}. \quad (4.54)$$

The final solution is therefore given by

$$\bar{u}(r) = ZH \left(\frac{I_o(\kappa r)}{I_o(\kappa b)} - \frac{I_o(\lambda r)}{I_o(\lambda b)} \right),$$

$$Z = \frac{1}{\lambda^2 - \kappa^2},$$

$$H = \frac{(\epsilon \epsilon_w \kappa^2 \psi_{wall} \nabla \phi)}{\mu}. \quad (4.55)$$

The Bessel functions in equation 4.55 will be approximately zero throughout the channel, except for very close to the channel wall. At the channel wall, the ratios of Bessel functions will both reach unity, cancelling each other out. This implies that electroosmotic force will cause the liquid to flow in the double layer near the channel wall, and viscous forces will cause the liquid outside the double layer to move as well. However, in this case, the drag induced on the fluid due to the uncharged spheres will prevent the viscous forces from reaching the center of the channel. Thus, only a

Figure 4.20: Flow profile in a porous cylinder with charged walls but an uncharged packing material for different porosities. The values $1/\kappa = 10nm$, $R = 125\mu m$, $d_p = 40\mu m$, $\psi_w = 40mV$, $E_z = 49200V/m$, $\eta = 5 \times 10^{-7}m^2/s$, $\rho_w = 1000kg/m^3$, $\tau = 2$, and $\epsilon_w = 4.2288 \times 10^{-10}$ were used.

Figure 4.21: Flow profile in a porous cylinder with charged walls but an uncharged packing material for different d_p values. The values $1/\kappa = 10nm$, $R = 10\mu m$, $\psi_{wall} = 40mV$, $E_z = 49200V/m$, $\eta = 5 \times 10^{-7}m^2/s$, $\rho_w = 1000kg/m^3$, $\tau = 2$, and $\epsilon_w = 4.2288 \times 10^{-10}$ were used.

thin layer of fluid close to the channel wall will move under an applied electric field. The thickness of this layer will depend upon the permeability of the medium and the thickness of the double layer. This is illustrated in figures 4.20 and 4.21, where the flow profiles are shown for different porosity and solid particle diameter values. It can be seen that the thickness of the fluid layer is very dependent upon the porosity. The presence of a high velocity fluid layer near the column wall could have serious implications on the performance of CEC columns in practice.

4.6.2 Steady porous flow in a charged medium with charged walls

The case in which both the packing material and the walls are charged can be considered by using the superposition of the individual cases. However, the ψ_{wall} term in equation 4.54 must be replaced by $\psi_{wall} - \psi_o$ to represent the difference in zeta potential on the wall relative to the zeta potential on the surface of the particles. This can be justified only when the zeta potential on either surface is small enough that the Poisson-Boltzmann equation can be linearized. Adding equations 4.54 and 4.45, the result is

$$\begin{aligned}\bar{u}(r) &= \frac{(\nabla P + \rho_{eff} \nabla \phi) K}{\mu \sqrt{\tau}} \frac{\eta}{\eta_e} \left(\frac{I_o(\lambda r)}{I_o(\lambda b)} - 1 \right) + ZH \left(\frac{I_o(\kappa r)}{I_o(\kappa b)} - \frac{I_o(\lambda r)}{I_o(\lambda b)} \right), \\ Z &= \frac{1}{\lambda^2 - \kappa^2}, \\ H &= \frac{(\epsilon \epsilon_w \kappa^2 (\psi_{wall} - \psi_o) \nabla \phi)}{\mu}.\end{aligned}\tag{4.56}$$

The volume flow is given by

$$U = \frac{\pi b^2 G K}{\mu \sqrt{\tau}} \frac{\eta}{\eta_e} \left[\frac{2I_1(\lambda b)}{\lambda b I_o(\lambda b)} - 1 \right] + 2ZH \left[\frac{I_1(\kappa b)}{\kappa b I_o(\kappa b)} - \frac{I_1(\lambda b)}{\lambda b I_o(\lambda b)} \right].\tag{4.57}$$

A similar model was developed by Rathore and Horvath [23] to investigate the effects of zeta potential mismatches in CEC columns (see Section 2.3). Although their model did not explicitly mention the Brinkman equation, their model can be viewed as a Brinkman model. However, they used a different definition for the permeability, and instead of using the no-slip condition ($u = 0$) at the wall, they neglected the double

layer region and assumed that the velocity was fully developed (using Smoluchowski's equation (2.86)). Their result was

$$u(r) = -\frac{\epsilon_w \psi_o E}{\mu} \left[1 + \frac{I_o\left(\frac{r}{\sqrt{K}}\right)}{I_o\left(\frac{b}{\sqrt{K}}\right)} \left(1 - \frac{\psi_w}{\psi_o}\right) \right]. \quad (4.58)$$

Figure 4.22: Intrinsic velocity profile in a porous cylinder with charged walls and a charged packing material. The values $d_p = 200\text{nm}$, $b = 1\mu\text{m}$, $1/\kappa \approx 2\text{nm}$, $\epsilon = 0.4$, $E_z = 49200\text{V/m}$, $\eta = 5 \times 10^{-7}\text{m}^2/\text{s}$, $\rho_w = 1000\text{kg}/\text{m}^3$, $\tau = 2$, $\psi_{wall} = 40\text{mV}$, $\psi_o = 20\text{mV}$, and $\epsilon_w = 4.2288 \times 10^{-10}$ were used.

The results of the two models are compared in Figure 4.22. The permeability from equation 2.42 was used for both models. As Rathore and Horvath's model is not volume-averaged, equation 4.56 was multiplied by $\frac{\sqrt{\tau}}{\epsilon}$ to obtain the intrinsic fluid velocity in the medium. Similarly, equation 4.58 was divided by $\sqrt{\tau}$ to account for the effect of the tortuosity on the electric field. Additionally, the double layer effects in the individual pores have been neglected in Rathore and Horvath's model. For the results in Figure 4.22, the solid particle diameter, d_p , was 200 nanometers, while the Debye layer thickness, $1/\kappa$, was approximately 2 nanometers. The κa ratio is

therefore only approximately 19 in this model (using equation 2.39 to find the average pore size, a), and as a result, the predicted channel velocity from equation 4.56 is lower than predicted by Rathore and Horvath's model. The size of the boundary layer near the wall will also be slightly different due to the incorporation of a few more terms in λ in equation 4.56 compared to the $1/\sqrt{K}$ dependence in Rathore and Horvath's model. Finally, it can be seen that neglecting the double layer region near the wall will overestimate the wall effect on the fluid velocity. Although the b and d_p values used here are smaller than would typically be used in a practical CEC system, the b/d_p ratio used is on the low end of those used in CEC. The values were chosen simply to facilitate viewing of the boundary layer near the wall by reducing the κb ratio.

The analogous solution for electroosmotic flow in a charged medium between two charged parallel plates is given by

$$\begin{aligned}\bar{u}(y) &= \frac{(\nabla P + \rho_{eff} \nabla \phi) K}{\mu \sqrt{\tau}} \frac{\eta}{\eta_e} \left(\frac{\cosh(\lambda y)}{\cosh(\lambda b)} - 1 \right) + ZH \left(\frac{\cosh(\kappa y)}{\cosh(\kappa b)} - \frac{\cosh(\lambda y)}{\cosh(\lambda b)} \right), \\ Z &= \frac{1}{\lambda^2 - \kappa^2}, \\ H &= \frac{(\epsilon \epsilon_w \kappa^2 (\psi_{wall} - \psi_o) \nabla \phi)}{\mu}.\end{aligned}\tag{4.59}$$

The model used in this section has two major drawbacks. First, the model assumes that the zeta potentials involved are small (less than 50 mV), so that the Poisson-Boltzmann equation can be linearized. In practical CEC systems, the column zeta potential can exceed 100 mV. Second, the model does not account for the fact that the porosity increases close to the wall due to packing inefficiencies. Both problems will be tackled in a later chapter using finite element analysis. However, a modification to the current analytical model can be used to estimate the effect of a higher porosity region near the channel wall. This will be done in the next section.

4.6.3 Zeta Potential Mismatches in a Cylinder with Two Porous Regions

Al-Hadhrami et al. [66] solved the Brinkman equation in rectangular and cylindrical channel geometries for pressure-driven flow. They also solved the Brinkman equation in channels with two or more adjacent regions of different porosity. Their method will be applied here to model electroosmotic flow in a cylinder with an inner region of radius b and porosity ϵ_1 and an outer region of porosity ϵ_2 located between b and c , in the case of charged walls and a charged packing material. This is illustrated in Figure 4.23. The Brinkman equation will be solved in each of these regions, with the requirement that the volume-averaged velocities match at the interface of the two regions. In addition, the continuity of the shear stress between the two regions will be ensured by the following equation, as suggested by Al-Hadhrami et al [66]:

$$\frac{\partial \bar{u}_1}{\partial r} = \frac{\eta_{e2}}{\eta_{e1}} \frac{\partial \bar{u}_2}{\partial r}. \quad (4.60)$$

Here, the subscripts 1 and 2 refer to the inner and outer regions, respectively. The flow in each region will be governed by the following Brinkman equation:

$$\begin{aligned} r^2 \frac{\partial^2 \bar{u}_n}{\partial r^2} + r \frac{\partial \bar{u}_n}{\partial r} - r^2 \lambda_n^2 \bar{u}_n &= -H_n r^2 \frac{I_o(\kappa r)}{I_o(\kappa c)} + r^2 \epsilon_n \frac{(\nabla P + \rho_{effn} \nabla \phi)}{\mu}, \\ H_n &= \frac{(\epsilon_n \epsilon_w \kappa^2 (\psi_{wall} - \psi_o) \nabla \phi)}{\mu}. \end{aligned} \quad (4.61)$$

Figure 4.23: Geometry used in the model of a cylinder with two different porous regions.

This is once again a Bessel equation, and the solution will therefore be given by

$$\begin{aligned}
\bar{u}_1(r) &= AI_o(\lambda_1 r) + Z_1 H_1 \frac{I_o(\kappa r)}{I_o(\kappa c)} - f_1 \\
\bar{u}_2(r) &= CI_o(\lambda_2 r) + DK_o(\lambda_2 r) + Z_2 H_2 \frac{I_o(\kappa r)}{I_o(\kappa c)} - f_2 \\
f_n &= \frac{\epsilon_n G_n}{\lambda_n^2 \mu}, Z_n = \frac{1}{\lambda_n^2 - \kappa^2} \\
n &= 1 \text{ for } r < b \\
n &= 2 \text{ for } b < r \leq c,
\end{aligned} \tag{4.62}$$

where the K_o term in the first equation has been dropped so that the velocity remains finite at $r = 0$. With the boundary conditions $\bar{u}_1(b) = \bar{u}_2(b)$, $\bar{u}_2(c) = 0$, as well as that given by equation 4.60, there are three equations with three unknowns. In general, there will be $2n - 1$ equations and $2n - 1$ unknowns for n regions of different porosity. In this analysis, n will be limited to two, because the algebra quickly becomes cumbersome for $n > 2$, and the matrices involved are very close to singular. Carrying out the algebra, the result for $n = 2$ is

$$\begin{aligned}
D &= \frac{f_2 \left[g \left(1 - \frac{I_o(\lambda_2 b)}{I_o(\lambda_2 c)} \right) + \frac{I_1(\lambda_2 b)}{I_o(\lambda_2 c)} \right] - g f_1 + W}{K_1(\lambda_2 b) + g \left(K_o(\lambda_2 b) - K_o(\lambda_2 c) \frac{I_o(\lambda_2 b)}{I_o(\lambda_2 c)} \right) + K_o(\lambda_2 c) \frac{I_1(\lambda_2 b)}{I_o(\lambda_2 c)}} \\
C &= \frac{f_2 - Z_2 H_2 - DK_o(\lambda_2 c)}{I_o(\lambda_2 c)} \\
A &= \frac{CI_o(\lambda_2 b) + DK_o(\lambda_2 b) + (f_1 - f_2) + \Theta_o}{I_o(\lambda_1 b)} \\
g &= \frac{\eta_{e1} I_1(\lambda_1 b) \lambda_1}{\eta_{e2} I_o(\lambda_1 b) \lambda_2} \\
\Theta_o &= (Z_2 H_2 - Z_1 H_1) \frac{I_o(\kappa b)}{I_o(\kappa c)} \\
\Theta_1 &= \frac{I_1(\kappa b)}{I_o(\kappa c)} \frac{\kappa}{\lambda_2} \left[\frac{\eta_{e1}}{\eta_{e2}} Z_1 H_1 - Z_2 H_2 \right] \\
W &= \left(g \frac{I_o(\lambda_2 b)}{I_o(\lambda_2 c)} - \frac{I_1(\lambda_2 b)}{I_o(\lambda_2 c)} \right) Z_2 H_2 - \Theta_1 - g \Theta_o.
\end{aligned} \tag{4.63}$$

If the porosity of each region is the same, equations 4.62 and 4.63 will reduce to

equation 4.56, while setting the difference in zeta potentials to zero will match the solution to equation 4.61 without the wall effect terms, given by Al-Hadhrami et al [66]. The effect of a region of higher porosity near the channel wall is illustrated in Figures 4.24 and 4.25. In Figure 4.24, the wall effect in a cylinder with two regions of porosity is compared to the wall effect in a cylinder with uniform porosity throughout. It is evident that the higher porosity near the wall increases the volume flow near the wall. In Figure 4.25, the volume-averaged velocity in a cylinder with two regions of porosity with and without a wall potential is shown. It can be seen that most of the increase seen in the volume flow near the wall is due to the higher zeta potential at the wall rather than the higher porosity alone.

Figure 4.24: Flow profile in a porous cylinder with charged walls and a charged packing material with two different porosity regions, compared with a cylinder with only one homogenous porous region. The values $d_p = 41\mu m$, $b = 110\mu m$, $c = 125\mu m$, $1/\kappa = 5nm$, $\epsilon_1 = 0.4$, $\epsilon_2 = 0.6$, $E_z = 40000V/m$, $\eta_{e1} = \eta_{e2} = 5 \times 10^{-7}m^2/s$, $\rho_w = 1000kg/m^3$, $\tau = 2$, $\psi_{wall} = 40mV$, $\psi_o = 20mV$, and $\epsilon_w = 40\epsilon_o$ were used.

The volume flow can be found by integrating $\bar{u}_1(r)$ from 0 to b and $\bar{u}_2(r)$ from b to c

Figure 4.25: Flow profile in a porous cylinder with charged walls and a charged packing material with two different porosity regions, with and without a wall potential. The values $d_p = 41\mu m$, $b = 110\mu m$, $c = 125\mu m$, $1/\kappa = 5nm$, $\epsilon_1 = 0.4$, $\epsilon_2 = 0.6$, $E_z = 40000V/m$, $\eta_{e1} = \eta_{e2} = 5 \times 10^{-7}m^2/s$, $\rho_w = 1000kg/m^3$, $\tau = 2$, $\psi_{wall} = 40mV$, $\psi_o = 20mV$, and $\epsilon_w = 40\epsilon_o$ were used.

in equation 4.62 and summing the result. The solution is

$$\begin{aligned}
 U = & \pi c^2 \left[\frac{2(CI_1(\lambda_2 c) - DK_1(\lambda_2 c))}{\lambda_2 c} + \frac{2Z_2 H_2 I_1(\kappa c)}{\kappa c I_o(\kappa c)} - f_2 \right] - \\
 & \pi b^2 \left[2 \left(\frac{CI_1(\lambda_2 b) - DK_1(\lambda_2 b)}{\lambda_2 b} \right) - 2A \frac{I_1(\lambda_1 b)}{\lambda_1 b} + \frac{2(Z_2 H_2 - Z_1 H_1) I_1(\kappa b)}{\kappa c I_o(\kappa c)} + \right. \\
 & \left. (f_1 - f_2) \right]
 \end{aligned} \tag{4.64}$$

A comparison of the volume flow for some of the different models for a cylindrical channel of radius $125\mu m$ is shown in Figure 4.26. The volume flow results are normalized with respect to the Darcy volume flow (4.1), i.e. the volume flow that would result if all boundary layers and wall effects are neglected. The volume flow for the Brinkman equation was found by using equation 4.46, while the volume flow for the case of a mismatched zeta potential only was found by using equation 4.57.

It can be seen that neglecting the porosity variation as well as the higher zeta potential at the wall can significantly underestimate the volume flow. In practical CEC columns, the zeta potential at the wall can exceed $100mV$, while the typical particle zeta potential can be less than $40mV$. The porosity variation seen in actual columns typically exhibits a sinusoidal variation near the wall that exponentially diminishes in magnitude to reach a constant value a few particle diameters away from the wall. This is a much more complicated phenomenon than can be captured by the two region model. Such effects will be considered in the next chapter using a numerical model.

Figure 4.26: Comparison of the volume flow in a porous cylinder using various models for a range of solid particle diameter values. The results are normalized with respect to the Darcy volume flow (equation 4.1). The values $b = 110\mu m$, $c = 125\mu m$, $1/\kappa = 5nm$, $\epsilon_1 = 0.4$, $\epsilon_2 = 0.6$, $E_z = 40000V/m$, $\eta_{e1} = \eta_{e2} = 5 \times 10^{-7}m^2/s$, $\rho_w = 1000kg/m^3$, $\tau = 2$, $\psi_{wall} = 40mV$, $\psi_o = 20mV$, and $\epsilon_w = 40\epsilon_o$ were used.

4.7 Conclusions

In this chapter, a number of analytical results were derived using different approximations of the generalized porous medium equation, in order to obtain a better understanding of the model. In particular, the Darcy and Brinkman models were investigated, as these two models should be applicable in most applications of interest to microfluidics designers.

In most practical applications, the flow velocity and the Darcy number will be small enough that the nonlinear terms and the viscous force term in the generalized porous medium equation can be neglected, resulting in a Darcy model for electroosmotic flow. A one-dimensional Darcy model was applied to a number of different geometries with different electrode configurations that might be of interest in microfluidic devices. It was found that in the Darcy regime, fluid flow can be modelled using Kirchhoff's Laws by assigning different regions a fluidic resistance. The effect of load regions, where there is no applied electric field, was investigated, and the Darcy model results were compared with numerical results. It was found that the one-dimensional Darcy model was accurate provided that there were no sudden changes in cross-sectional area in the electroosmotic pump (the region with the applied electric field). A model describing the flow in different arms of a two-channel intersection was also presented. Although the one-dimensional Darcy model was able to predict the flow in the channel arms fairly accurately, valuable information, such as the flow profile at the intersection, is lost in the model.

The effects of incorporating the viscous force term through the Brinkman equation was investigated next. For the case of a porous medium with uncharged walls, it was found that a very thin boundary layer exists near the channel wall where the fluid velocity rapidly drops to zero. The thickness of this region was found to be proportional to the square root of the permeability. The solution to the Brinkman equation was found for flow between two parallel plates, in a cylinder, and in a rectangular channel. The boundary layer, in practice, need only be considered if the ratio of the average pore size to the channel width is relatively large.

The time-dependent Brinkman equation for flow between two parallel plates was solved in order to estimate the amount of time required for the fluid velocity to reach steady state. It was found that the time constant was proportional to $\frac{a^2}{8\eta_e}$, which will typically be in the range of a few nanoseconds to microseconds. Thus, in most practical situations, it will be possible to assume that the fluid flow reaches steady state instantaneously.

Two different wall effects that are seen in capillary electrochromatography (CEC) columns were investigated. First, the effects of a zeta potential mismatch between the charged particles and the column wall was investigated, assuming that the zeta potentials were small enough that the Poisson-Boltzmann equation can still be linearized. Then, the combined effects of an increased porosity near the column wall as well as a zeta potential mismatch was considered. It was found that both effects combined can have a significant impact on the volume flow in the channel.

Although the above model could be used to estimate the effects that might be seen in a practical CEC column, it neglects the fact that the zeta potentials at the wall can exceed $100mV$, which is in the regime where nonlinear effects must be considered in the Poisson-Boltzmann equation. It also over-simplifies the behaviour of the porosity near the column wall due to packing inefficiencies. Furthermore, many researchers use porous particles in their CEC columns. These pores are usually only a few nanometers wide, and thus, for pressure-driven columns, it is usually assumed that the pressures used are not sufficient to force liquid through the small pores. However, in electroosmotic flow, it will be seen that the velocity of the fluid in the porous particles can reach a substantial fraction of the fluid velocity in the rest of the column. These issues will be addressed in the next chapter, and the numerical results of the models will be compared with experimental results from the literature.

Chapter 5

Theoretical and Experimental Comparisons

In this chapter, the theory derived in the previous chapters is validated by comparing numerical modelling results with experimental results from the capillary electrochromatography (CEC) literature and with experiments performed with devices made from nitrocellulose membranes. It will be found that the theory is capable of matching the experimental results, although, due to the many difficulties encountered when interpreting experimental electroosmotic flow data in porous media, there will likely be more than one parameter set capable of fitting the data. However, due to the complexity of the models used to simulate the experimental data, the agreement of the models with experiment is encouraging.

In chromatography applications, different analytes can be separated from one another using a number of different techniques; researchers are continually looking for ways to enhance resolution while reducing the analysis time. In many chromatography applications, the packing material is responsible for much of the separation resolution that is achieved. The surface properties of the material can be altered using different buffer solutions so that specific analytes will be attracted to the surface, slowing them down relative to other analytes that are not attracted to the surface. In some applications, electric fields are used to provide more resolution by enhancing separation based upon the charge and molecular size of the different analytes. In capillary electrochromatography (CEC), one segment of a cylindrical column is packed with spheres. Electroosmosis is used to drive the fluid (and thus the analytes) through the packed segment towards a detection window, which is usually located in

an open segment (see Figure 5.1).

Figure 5.1: Illustration of a typical capillary electrochromatography (CEC) column. One end of the column is usually packed with porous particles, which are held inside the column using retaining frits. The packed segment is usually followed by an open segment. Electroosmotic flow in the packed segment carries the analytes of interest to the detection window in the open segment. The separating properties of the medium will often be largely due to the surface chemistry of the particles.

In many chromatography applications, porous particles are used as the packing material, with particle pore sizes of only a few nanometers. Porous particles provide much more surface area upon which desired chemical reactions can take place. In pressure-driven flow applications, the pressures used in practice are typically not large enough to induce flow inside the particles' pores, and thus the transport of an analyte through the particles is dependent solely upon diffusion. This severely limits the maximum flow rate that can be used in chromatography applications, as higher flow rates do not afford the analyte enough time to diffuse fully through the particles' porous structure. However, if the transport is being driven by electroosmosis, it is quite possible that significant flow rates can be achieved in the very small pores in the particles, which would reduce the amount of time required for the analyte to perfuse through the particles. A model for flow in capillary electrochromatography columns that takes into consideration the flow in the porous particles themselves, as well as between the particles, will be compared with experimental data presented in Liapis and Grimes [2] in Section 5.1. It will be seen that the theory matches the experimental results, and predicts that, although only a small fraction of the volume flow occurs through the porous particles, the fluid flows through the particles at a significant fraction of the velocity of the fluid between the particles. These results are in keeping with the predictions of the models developed by Liapis and Grimes [2, 71].

One requirement for many chromatography applications is that the analyte of interest experience minimal dispersion, i.e. an initial band of solute must experience minimal spreading as it traverses the column. Electroosmotic flow helps to minimize spreading due to its relatively flat velocity profile in the individual pores, as well as the fact that the velocity in each pore is independent of the pore radius (unlike pressure-driven flow), provided that the Debye length-pore radius ratio is large ($\kappa a \gg 1$). However, the particle packing near the column wall is not as efficient as it is at the center of the column (see Figure 5.4(a) or 5.4(b)). Close to the wall, the porosity approaches a value of unity, which implies that the average pore size increases as the wall is approached, thereby increasing the average volume flow near the wall. This effect is exacerbated in pressure-driven flow due to dependence of the velocity on the pore radius. In electroosmotic flow, the zeta potential of the column wall is often much higher than the zeta potential of the packing particles, leading to increased volume flow near the column wall, which is exacerbated by the higher porosity in this region. These effects are examined for electroosmotic flow and compared with the experimental data provided in Tallarek et al [3] in Section 5.2. It will be seen that the theory can match the concentration profiles seen by Tallarek et al quite well, although evidence exists of additional effects (such as thermal effects, pressure gradients, and dispersion effects) not considered by the model.

Finally, simple microfluidic devices are built using porous nitrocellulose membranes, and the theory is used to match the experimental results in Section 5.3. In order to obtain a qualitative fit to the experimental results, it will be seen that the model needs to incorporate an anisotropic permeability in the porous membranes and electrochemical effects that result in a decline of the electric field over time. Although such effects can be included into the model empirically, truly predictive models for analyte transport due to electroosmotic flow in porous materials will need to include a more rigorous treatment of the electrochemical problem. In addition, due to the number of unknowns in the experimental data, in order to reduce the ambiguity of experimental results, future experiments must be carefully designed to help reduce the number of unknowns.

5.1 Comparison with experiments of Liapis and Grimes

A model for electroosmotic flow applied to capillary electrochromatography was developed by Liapis and Grimes [2]. In their model, the packed column was assumed to be composed of a large number of tortuous capillaries. The Poisson-Boltzmann equation was solved numerically to determine the charge density profile in a single pore, from which the average volume flow through a single pore could be calculated. The average flow speed for the entire column was assumed to be given by the average flow through a single pore multiplied by a conductivity term that incorporates the effects of tortuosity. Their model therefore determines the *intrinsic* average speed of the fluid in the pores, rather than the *volume-averaged* flow, which is the effective speed of the fluid required to yield the actual volume flow. It was shown in section 2.1.1 that the two are related by

$$u_{ave} = \bar{u} \frac{A}{A_e} = \bar{u} \frac{\sqrt{\tau}}{\epsilon}, \quad (5.1)$$

where u_{ave} denotes the intrinsic average flow velocity and $\bar{u}$ denotes the volume-averaged velocity.

Liapis and Grimes [2] next compared the results of their model with experiments performed by K.K. Unger and S. Ludtke. The data obtained by Unger presented in Liapis and Grimes [2] will be used to validate the model developed in this work.

Unger measured the flow velocity in a column of radius $50\mu m$, packed with porous silica C8 particles with diameters of 0.5, 1.0, and $3.0\mu m$ [2]. Measurements performed by Ludtke on porous silica C8 particles of $0.5\mu m$ diameter with a mobile phase of 80% acetonitrile, 20% 25 mM TrisHCl at pH 8.0 and temperature $20^\circ C$ found the zeta potential at the surface of the particles to be $-64.1 mV$ [2]. The zeta potential at the column wall was assumed to be the same as the zeta potential of the particles. Unfortunately, few details about how these measurements were performed were provided. Zeta potential measurements are usually extracted from streaming potential or electroosmotic flow experiments, and thus will depend on the model for

electroosmotic flow that was used. It is unlikely that the model used to calculate the zeta potential accounted for the possibility of flow through the porous particles themselves. It is conceivable that a small but appreciable fraction of the volume flow occurs through the particles, which could change the interpretation of the zeta potential measurements. The effects of this small fraction of volume flow through the particles will be discussed below in Section 5.1.2.

Variable	Symbol	Value	Variable	Symbol	Value
bed porosity	ϵ	0.35	permittivity	ϵ_w	$4.23 \times 10^{-10} \text{ F/m}$
bed tortuosity*	τ	1.95	inverse Debye length	κ	$1/1.488 \text{ nm}$
zeta potential	ψ_o	-64.1 mV	coeff of viscosity	μ	$4.99 \times 10^{-4} \text{ Pa s}$

Table 5.1: Experimental data provided by Liapis and Grimes [2]. Values with an asterisk are estimated.

The experimental parameters provided by Liapis and Grimes are shown in Table 5.1. In their model, the pore velocity was weighted by a conductivity term to represent the tortuosity of the medium, similar to that given in equation 2.89. They found that using a value of 0.716 provided a good fit for the data, which would correspond to a tortuosity value, τ , of 1.95.

5.1.1 Modelling Flow Through Columns Packed with Non-porous Particles

The theory developed here will first be used to model the flow in the column, in the case where the flow in the porous particles is neglected. Later, the model will be expanded to include the porosity of the particles. Using the values provided in Table 5.1, the permeability of each column can be calculated using equation 3.16. Assuming that the pore shape factor k_o is 2, the permeabilities for the columns with particle diameters of 0.5, 1.0, and 3.0 μm are $7.2 \times 10^{-16} \text{ m}^2$, $28.8 \times 10^{-16} \text{ m}^2$, and $259.5 \times 10^{-16} \text{ m}^2$, respectively. The Brinkman screening length, $1/\lambda$, defined by equation 4.28, for each column is therefore given by 38.4 nm, 76.8 nm, and 230.4 nm, respectively, where it has been assumed that the effective viscosity of the fluid is identical to the actual viscosity. Noting that the diameter of the columns is $2b = 100 \mu\text{m}$, the λb ratios can be seen to be much greater than one, allowing one to neglect the boundary layer effects near the column wall. The electroosmotic flow in the column can therefore be

modelled using the Darcy approximation (4.1).

The average pore size between the particles can be estimated from equation 2.39, which yields 89.7 nm , 179.5 nm , and 538.5 nm for the particle diameters of 0.5 , 1.0 , and $3.0\text{ }\mu\text{m}$, respectively. Liapis and Grimes estimated that the average pore radius is approximately one third the particle radius, which would yield similar results. Since the Debye length is approximately 1.488 nm , the κa ratios will be large, and thus the boundary layer effects in the individual pores will be small.

The complete, nonlinear Poisson-Boltzmann equation (2.55, 2.56) was solved numerically in Femlab using a one dimensional axisymmetric model. The initial mesh size at the wall was chosen to be $1 \times 10^{-12}\text{ m}$ with a growth rate of 1.001. For the smallest pore size, this resulted in a mesh with a total of approximately 4500 elements, of which about 1700 would lie within the Debye region (see Appendix 7.3 for details). The effective charge density was calculated using equation 3.18. The required numerical integration over the potential profile was performed using a trapezoidal rule. Finally, the results were scaled by the porosity and the square root of the tortuosity, to find the intrinsic average pore velocity (rather than the volume-averaged velocity). The numerical results are compared with the experimental results in Figure 5.2. It can be seen that the model matches the experimental data fairly well, and is virtually identical to the results of the model developed by Liapis and Grimes [2]. Note that the zeta potential used here is only slightly greater than 50 mV , and thus there would be only a minor difference in the results if the analytical model rather than the full nonlinear numerical model had been used.

As mentioned earlier, this model takes no account of the fact that the particles themselves are porous. However, calculations made by Liapis and Grimes indicated that the Debye length-pore radius ratios in the pores of the particles were high enough to permit the possibility of flow through the porous particles. They investigated this problem further in later articles, such as in reference [71], where they employed network models to investigate the influence of the flow through the porous particles on the total flow. These models indicated that the contribution of the porous particles

Figure 5.2: Comparison of theoretical results with the experimental results provided in Liapis and Grimes [2], neglecting flow through the porous particles, with $\psi_o = -64.1mV$. See Table 5.1 for the values used.

would contribute to somewhere between a fraction of a percent and a few percent of the total flow, depending on the degree of interconnectedness of the pores.

5.1.2 Modelling Flow Through Columns Packed with Porous Particles

The theory proposed in this work will now be used to model flow through the capillary column with porous particles. This model is simpler to use than theories invoking network models; in fact, it is an analytical model provided the zeta potentials involved are not too large. This makes the model more accessible to researchers who are hoping to optimize their chromatography columns without developing complicated modelling software.

The pores within the particles will be modelled as a fluidic resistance in parallel with the resistance provided by the pores between the particles. According to Liapis and Grimes' network models, the porosity of the particles, ϵ_p , is approximately 0.49, while the average pore size, a_p , is approximately 11.51 nm. The effective solid particle

diameter of a porous medium was given by equation 2.38. The effective solid particle diameter for the pore network within the porous particles, d_{pp} , which will be used to calculate the permeability of the particle, can therefore be found in a similar fashion. Using the values of 0.49 for ϵ_p and 11.51 nm for a_p , the calculated value for d_{pp} was 35.94 nm.

The effective porosity of the particle, ϵ_{pe} , is defined as

$$\epsilon_{pe} = (1 - \epsilon)\epsilon_p, \quad (5.2)$$

which takes into account the fact that the particles themselves take up $(1 - \epsilon)$ of the volume of the column. The total porosity of the column is given by

$$\epsilon_{tot} = \epsilon + \epsilon_{pe} = \epsilon + (1 - \epsilon)\epsilon_p. \quad (5.3)$$

In order to calculate the average volume flow through the column, one must take into consideration the volume flow contributions from the interparticle and intraparticle pores. By definition, the permeability of a porous medium is the resistance seen by a fluid that results in a volume-averaged flow velocity for an applied pressure gradient (see equation 2.7). Because there is more than one pore size, the permeability of the interparticle and intraparticle flows must be weighted by the average cross-sectional area of the pores in question, as well as the fraction of void volume that they include. By referencing Darcy's Law for electroosmotic flow (4.1), the average volume flow can therefore be found to be the following:

$$\bar{u} = \frac{G}{\sqrt{\tau}\mu} \left[\frac{\frac{K_{peff}}{\sqrt{\tau}}\pi a^2 \left(\frac{\epsilon}{\epsilon_{tot}}\right) + \frac{K_p \rho_{effp}}{\sqrt{\tau_p}}\pi a_p^2 \left(\frac{\epsilon_{pe}}{\epsilon_{tot}}\right)}{\pi a^2 \left(\frac{\epsilon}{\epsilon_{tot}}\right) + \pi a_p^2 \left(\frac{\epsilon_{pe}}{\epsilon_{tot}}\right)} \right], \quad (5.4)$$

where the subscript p denotes the corresponding value for the intraparticle pores in the porous particles. The permeability K_p can be calculated using ϵ_p , d_{pp} , and τ_p in equation 3.16. The value of 1.65 used for the tortuosity τ_p was obtained from reference [3]. The intrinsic average velocity can be found by scaling by the corresponding values

of ϵ and τ , resulting in

$$u_{ave} = \frac{G}{\sqrt{\tau}\mu} \left[\frac{\frac{K_{eff}}{\epsilon_{tot}} \pi a^2 + \frac{K_{p,eff,p}}{\epsilon_{tot}} \pi a_p^2}{\pi a^2 \left(\frac{\epsilon}{\epsilon_{tot}} \right) + \pi a_p^2 \left(\frac{\epsilon_p}{\epsilon_{tot}} \right)} \right]. \quad (5.5)$$

Variable	Symbol	Value	Variable	Symbol	Value
bed porosity	ϵ	0.35	particle porosity	ϵ_p	0.49 [71]
bed tortuosity*	τ	1.95	particle tortuosity*	τ_p	1.65 [3]
coeff of viscosity	μ	$5 \times 10^{-4} \text{ (kg/m}^3\text{)(m}^2\text{/s)}$	particle pore radius	a_p	11.51 nm
permittivity	ϵ_w	$4.23 \times 10^{-10} \text{ F/m}$	inverse Debye length	κ	1/1.49 nm

Table 5.2: Data used to match the experimental data from Liapis and Grimes [2], taking into consideration the porosity of the particles. Values with an asterisk are estimated.

The effective charge densities were calculated numerically, as in the case considered above for the column with particles that were not porous. The values used in the model are shown in Table 5.2. The final results are compared with the experimental results in Figures 5.3(a) and 5.3(b) for a zeta potential of -64.1 and -63.1 mV, respectively. By comparing Figure 5.2, the case where the particles were not porous, and Figure 5.3(a), where the particles' porosity has been taken into consideration, it can be seen that the flow through the porous particles has only a minor effect on the total flow. However, it can be seen in Figure 5.3(a) that the predicted flow rates are slightly higher. The use of a slightly lower zeta potential of -63.1 mV can lower the flow rate to better fit the experimental data, and better match the theoretical data of the non-porous case. This has been illustrated in Figure 5.3(b).

The fraction of the volume flow through the intraparticle pores was determined by calculating the ratio of the K_p portion of equation 5.4 to the total volume flow. The intraparticle volume flow was found to be 1.95%, 0.49%, and 0.05% of the total volume flow for the particle diameters of 0.5, 1.0, and 3.0 μm , respectively. Thus, the intraparticle flows are almost negligible, although effects become more significant for smaller particle diameters. Small ratios of intraparticle to total volume flow were also predicted by the network modelling of Liapis and Grimes [71]. Note that this does not necessarily mean that the fluid velocity in the intraparticle pores is negligible; the ratio of intraparticle to interparticle velocities (found using equations 4.1 and 5.1 for each pore size) is actually 0.8741, 0.8608, 0.8521, indicating that the fluid in the

Figure 5.3: Comparison of theoretical results with the experimental results provided in Liapis and Grimes [2], taking the flow through the porous particles into consideration. See Table 5.2 for the values used.

porous particles is moving almost as fast as the fluid outside the pores. The small fraction of the volume flow is simply due to the small volume of the particle pores.

5.1.3 Conclusion

The model for electroosmotic flow in porous media developed here can be used to reproduce volume flow data taken from CEC experiments. The agreement between theory and experiment is quite good, although many effects have been neglected, such as the increase in temperature induced by the high electric fields employed in CEC, or changes in the dielectric constant or zeta potential that can arise due to an unequal distribution of the buffer solution, or its absorption by the wall and particles.

The above analysis has also demonstrated that it is possible to obtain a rough estimate of the magnitude of the intraparticle flows in CEC columns using the simple model developed here. It has been shown that zeta potential measurements inferred from electrokinetic measurements may have to take the porosity of the particles into account as well, although this effect is expected to be small in most cases. In practice,

the pore size in the porous particles will have a statistical distribution which could significantly affect the intraparticle flow rate. This model has also neglected the degree of connectivity of the pores in the particles, as well as any polarization effects that might occur due to different pore orientations relative to the applied electric field. This model could be modified in future work to take such effects into consideration.

5.2 Comparison with experiments of Tallarek et al.

As mentioned previously, there are two wall effects that can affect the performance of chromatography columns: a difference in zeta potential between the column wall and the packing material, and an increase in porosity near the wall due to packing inefficiencies. Simple models for both were developed in Section 4.6. Unfortunately, analytical solutions are not possible if the zeta potentials involved become large, which happens to be the case for many CEC columns. In addition, the analytical model for the porosity increase near the wall used a step increase in the porosity (see Section 4.6). In practice, the porosity is an oscillating, decreasing function of position away from the wall, with a maximum of close to unity near the column wall. In order to incorporate both these effects, a numerical model is required. In this section, a numerical model that incorporates both effects will be considered. First, experimental data from the literature for the porosity variation near the boundary wall will be presented. Then, the numerical model will be compared with the analytical models from the previous chapter. Finally, the numerical model will be used to fit the experimental concentration profiles obtained by Tallarek et al [3] for a CEC column.

5.2.1 Porosity Variations Near the Column Wall

Experimental data illustrating the porosity variations near the column wall, originally obtained by Benenati and Brosilow, were presented in Tallarek et al [4] for two different ratios of column to particle diameter. This data is shown again here in Figures 5.4(a) and 5.4(b), along with a plot of an empirical expression for the average porosity

variation provided by Nield and Bejan [27]. It can be expressed as

$$\epsilon(r) = A_o \left(1 + C_o \exp^{-\frac{N(b-r)}{d_p}} \right). \quad (5.6)$$

Nield and Bejan [27] suggested using the values 0.4, 1.4, and 5 for the parameters A_o , C_o , and N , respectively. These values have been used in Figures 5.4(a) and 5.4(b), and it can be seen that the expression fits both sets of data quite well. The oscillating porosity near the wall is due to the varying probability that a solid particle is located at a particular position from the column wall. The local minima in the porosity occur at positions where a solid particle is most likely to appear, and thus are located approximately one solid particle diameter apart.

Another model that has been found empirically to approximate the porosity variation can be given by

$$\epsilon(r) = A_o + B J_o \left(\frac{C(b-r)}{d_p} \right) - D J_1 \left(\frac{Er}{d_p} \right), \quad (5.7)$$

where A_o is the porosity value far from the column wall, B, C, D , and E are parameters that must be used to fit the expression to the data, and J_n are Bessel functions of the first kind of order n . Plots of this function for the two different data sets are given in Figures 5.5(a) and 5.5(b). For the $R = 2.8d_p$ case, the values of 0.39, 0.45, 7.03, 0.042, and 6 were used for A_o, B, C, D , and E , respectively. For the $R = 7.05d_p$ case, the values of 0.39, 0.42, 4.8, 0.1, and 5.08 were used. These values were chosen by minimizing the sum squared error between equation 5.7 and the data.

5.2.2 Numerical comparison of the full equation and the Brinkman equation

In section 3.2, the nonlinear terms in the generalized porous medium equation were shown to be important only when the modified Reynolds number is large, or if the velocity becomes large enough that the nonlinear Forchheimer term becomes important. It is usually safe to assume that the nonlinear terms can be neglected in pure electroosmotic flow, as it is usually not practical to use electric fields of the magnitude

(a) $R=2.8 d_p$ (b) $R=7.05 d_p$

Figure 5.4: Experimental data for porosity variation and the averaged porosity (equation 5.6) in a column with $R = 2.8 d_p$ and $R = 7.05 d_p$.

(a) $R=2.8 d_p$ (b) $R=7.05 d_p$

Figure 5.5: Experimental data for porosity variation and the approximate porosity using the Bessel function model (equation 5.7) in a column with $R=2.8 d_p$ and $R=7.05 d_p$.

required to accelerate the fluid enough to produce the nonlinear effects. However,

these effects may become significant in combined pressure-driven and electroosmotic flows.

Figure 5.6: Comparison of the numerical and analytical solutions for volume averaged flow in a cylindrical channel, in the case of an uncharged wall, with $\psi_o = -40$ mV, and a constant porosity of 0.4. Other variables are as in Table 5.3.

The effect of the nonlinear Forchheimer terms on the fluid velocity has been investigated using a model for CEC fluid flow, and can be seen in Figures 5.6(a) and 5.6(b). Here, the results of the analytical solution, the numerical solution to the Brinkman equation, as well as the numerical solution to the complete generalized porous medium equation are compared for a capillary electrochromatography column with constant porosity. The use of a relatively large electric field of 49200 V/m (as might be seen in CEC applications) is shown in Figure 5.6(a). It can be seen that all three solutions are in agreement, at an average volume flow rate of less than 0.15 mm/s. The critical velocity above which the Forchheimer term can no longer be neglected was defined in section 3.2 as

$$\overline{u}_{crit} \approx 0.01 \frac{\eta_e}{F_e \sqrt{K}}. \quad (5.8)$$

In this case, η_e is 8.9×10^{-7} m²/s, ϵ is 0.4, τ is 1.65, and d_p is 41 μ m. F_e , given by equation 3.17, is therefore 0.7193, and K is 3.23×10^{-12} m². It is therefore required that $\overline{u} < \overline{u}_{crit} = 6.883$ mm/s if the Forchheimer term is to be neglected. This is

certainly satisfied in this case. However, at much higher flow rates, such as would be generated by an electric field one hundred times higher (4.92 MV/m), neglecting all the complicating factors that such an unrealistically high electric field would cause, the Forchheimer term has a significant effect on the average volume flow. This is illustrated in Figure 5.6(b), where the volume flow rate reaches just less than 15 mm/s . Note that if the pore size increases dramatically, to over $100 \text{ }\mu\text{m}$, the critical velocity at which the Forchheimer term must be considered would drop considerably.

Figure 5.7: Comparison of the numerical and analytical solutions for volume averaged flow in a cylindrical channel, in the case of an uncharged wall, with $E_z = 49.2 \text{ kV/m}$ and $\psi_o = -40 \text{ mV}$, taking into consideration the porosity variation near the wall. Equation 5.7 was used for the porosity variation, using $A_o = 0.39$, $B = 0.49$, $C = 8$, $D = 0.05$, and $E = 7$. Other variables are as in Table 5.3.

In the following sections, the one dimensional Brinkman equation is used in a numerical model of CEC fluid flow, taking porosity variation into consideration. The use of the one dimensional Brinkman equation rather than its two dimensional counterpart or the full solution of the two dimensional generalized porous medium equation is validated in this section by comparing the numerical solutions of each. As seen in Figure 5.7, the one dimensional Brinkman model for flow in a packed column with large porosity variations is identical to either of the two dimensional models, in spite of the presence of velocity gradients across the channel radius, as the radial velocity components are still negligible. The axial flow velocity is still small enough that the

Forchheimer term can be neglected. The use of the one dimensional Brinkman equation instead of the two dimensional Brinkman equation is advantageous as it is much less memory intensive, permitting the use of a much denser mesh.

5.2.3 Full Solution to the Nonlinear Poisson-Boltzmann Equation

As the zeta potentials in CEC columns often exceed 50 mV , it is of interest to determine how the numerical solution of the complete nonlinear Poisson-Boltzmann equation (2.55) differs from the analytical solutions presented in Section 4.6, for the case where the porosity is constant across the channel.

In Section 4.6, the zeta potential at the column wall was modelled by $\psi_{wall} - \psi_o$ in order to represent the additional zeta potential contribution of the wall. This can be justified at low zeta potentials, because the Poisson-Boltzmann is still in the linear regime. However, at higher zeta potentials, this can no longer be justified, and so the potential distribution in the channel can be found by solving the Poisson-Boltzmann over the entire channel, once with $\psi_1(b) = \psi_{wall}$, and once with $\psi_2(b) = \psi_o$:

$$\begin{aligned}\nabla^2\psi_1 &= -\frac{e\sum_i^N n_i z_i e^{-\frac{e z_i \psi_1}{kT}}}{\epsilon_w} \\ \nabla^2\psi_2 &= -\frac{e\sum_i^N n_i z_i e^{-\frac{e z_i \psi_2}{kT}}}{\epsilon_w}.\end{aligned}\tag{5.9}$$

The charge distribution in the channel due to the charge on the wall can be approximated using the difference in potentials $\psi_1(r) - \psi_2(r)$ in equation 2.56 to obtain

$$\rho_{wall}(r) = -2n^o z e \sinh\left(\frac{ze(\psi_1(r) - \psi_2(r))}{kT}\right).\tag{5.10}$$

This can then be used in the Brinkman equation (4.40) to find the flow in the channel, which yields

$$\frac{\eta}{\sqrt{\tau}\epsilon} \frac{\partial^2 \bar{u}}{\partial r^2} + \frac{\eta}{\sqrt{\tau}\epsilon} \frac{1}{r} \frac{\partial \bar{u}}{\partial r} - \eta_e \frac{\bar{u}}{K} = \frac{(\nabla P + (\rho_{eff} + \rho_{wall}(r))\nabla\phi)}{\rho_w \sqrt{\tau}}.\tag{5.11}$$

It was assumed that the pores between the particles were large enough that the double layer regions could be neglected (with a d_p of $41\ \mu m$, the average pore size, a , is approximately $9\ \mu m$, while κ is less than $10\ nm$). Thus the effective charge density is given by

$$\rho_{eff} = -\frac{8\epsilon_w\psi_o}{a^2}. \quad (5.12)$$

These equations were solved using a one-dimensional axisymmetric application mode in Femlab, with a mesh of initial size $1 \times 10^{-14}\ m$ at the column wall and a growth rate of 0.01 to ensure that the mesh was fine enough near the wall. The solutions for a number of different zeta potentials are compared with the analytical solutions from Section 4.6 in Figures 5.8(a), 5.8(b), and 5.8(c). It can be seen that the numerical solutions deviate from the analytical solutions before the wall zeta potential reaches $50\ mV$. The discrepancy between the numerical and analytical solutions becomes quite pronounced for large zeta potential differences, as seen in Figure 5.8(c), which is very much in the nonlinear regime.

5.2.4 Numerical model for Tallarek's experimental data

Tallarek et al [3] used a stimulated echo version of pulsed-field gradient nuclear magnetic resonance (PFG-NMR) imaging to investigate the effects of intraparticle flows and mismatched zeta potentials in CEC columns. A column of radius $125\ \mu m$ was packed with porous particles with a mean diameter of $41\ \mu m$. A buffer solution of degassed sodium tetraborate with a pH of 9.13 was used in the columns, with a range of different concentrations. The NMR imaging scheme permitted the determination of the probability that any molecule had travelled a given displacement over the duration of the observation time. This can be considered to be a plot of the normalized concentration down the column length at time t (see Figure 5.10). It was found that much of the dispersion seen in pressure-driven flow was due to very low intraparticle flows. For pure electrokinetic flow, however, dispersion due to the intraparticle flows could not be isolated. The concentration profile was primarily Gaussian in shape, except for a noticeable fronting effect that was thought to be due to a mismatch in zeta potentials between the packing material and the column wall. This fronting effect, involving both porosity variation and zeta potential mismatches, will be modelled in

Figure 5.8: Comparison of the numerical and analytical solutions for flow in a cylindrical channel, with $\kappa = 1/2.34 \text{ nm}$ and constant porosity. Also shown for comparison is the model developed by Rathore and Horvath [23] (Section 2.3).

Femlab and compared with the experimental results of Tallarek et al.

The model used here is essentially the same as that used in the preceding section. However, it must be noted that the porosity is now a function of position. Thus, the

average pore size, a , is now also a function of position, as is the permeability, K , and the effective charge density, ρ_{eff} . It will be assumed that the concentration obeys the convection-diffusion equation (3.32)

$$D\nabla^2 C = \frac{\partial C}{\partial t} + u_{ave} \cdot \nabla C, \quad (5.13)$$

where u_{ave} is the intrinsic (not the volume-averaged) velocity of the fluid. The porosity and the tortuosity of the medium can be taken into consideration by using the same scaling for the tortuosity that was used in Section 2.1.4, and setting the effective concentration, $\bar{C}$, as $\bar{C} = \epsilon C$. The scaled convection-diffusion equation is therefore [27]

$$\frac{D}{\tau} \nabla^2 (\epsilon \bar{C}) = \frac{\partial (\epsilon \bar{C})}{\partial t} + \frac{u_{ave}}{\sqrt{\tau}} \cdot \nabla (\epsilon \bar{C}). \quad (5.14)$$

An approximate solution to this equation can be found if the transverse diffusion components are neglected. This approximation would neglect diffusion across streamlines, which would tend to reduce the dispersion seen by the concentration near the wall, where the fluid velocities are highest. If the transverse diffusion effects are neglected, the porosity in each term will cancel out, and the solution will be of the form

$$C(r, z, t) = \frac{C_o}{2\sqrt{\pi D_{eff} t}} \exp\left(\frac{-(z - \frac{u_{ave}(r)}{\sqrt{\tau}} t)^2}{4D_{eff} t}\right), \quad (5.15)$$

where z is the distance in the axial direction, and D_{eff} was taken to be equal to $\frac{D_m}{\tau}$. The total concentration at position z along the column could then be calculated by integrating over the radius of the column using

$$C(z, t) = \int_0^{2\pi} \int_0^R C(r, z, t) dr d\theta. \quad (5.16)$$

The numerical integration was performed using a trapezoidal rule. The values in Table 5.3 were used in order to model the data shown in Figure 7b of Tallarek et al [3]. In order to achieve an estimate of the particle zeta potential, ψ_o , streaming potential measurements were performed by Tallarek et al. over a range of different buffer concentrations. It was found that the buffer concentration had a large impact

on the particle zeta potential. For the concentration ranges used in their study, they found that the particle zeta potential was approximately between -8 and -10 mV, without taking the porosity or tortuosity of the column into account [3]. Because the double layer effects can be neglected, this can be accomplished, referring to equation 3.9, by dividing by the porosity and multiplying by the tortuosity. If the porosity at the center of the channel is approximately 0.39 and the tortuosity is between 1.65 and 2, the actual particle zeta potential should be somewhere in the range of -33 to -51 mV. From their data, Tallarek et al. estimated that the wall zeta potential, ψ_w , was at least three times greater than ψ_o [3]. Tallarek gave a value of 1.67 for the bed tortuosity for a channel with 50 μm particles in reference [4]. The permittivity of the fluid was determined by finding the ϵ_w required to fit equation 2.59 to the Debye length values for different concentration values given in Tables 1 and 2 of Tallarek [3], noting that there are two moles of charged species created for every mole of buffer solution in this case. The value for the kinematic viscosity was provided by Tallarek, but the value for the density of the fluid was estimated using the value given by Liapis and Grimes for their column [2], although a different buffer had been used in their work.

Figure 5.9: Comparison of the experimental data taken from Figure 7b of Tallarek [3] with the numerical model using a constant porosity and equations 5.15 and 5.16 for the concentration profile. The values $\psi_w = 135$ mV, $\psi_o = 38$ mV, $D_{eff} = 3.6 \times 10^{-9}$ m²/s, and $\tau = 1.65$ were used.

Figure 5.10: Comparison of the experimental data taken from Figure 7b of Tallarek [3] with the numerical model using equation 5.6 for the average porosity variation and equations 5.15 and 5.16 for the concentration profile. The values $\psi_w = 135 \text{ mV}$, $\psi_o = 38 \text{ mV}$, $D_{eff} = 3.6 \times 10^{-9} \text{ m}^2/\text{s}$, and $\tau = 1.65$ were used.

Variable	Symbol	Value	Variable	Symbol	Value
porosity (center)*	ϵ_o	0.4	buffer conc	C	0.001 M
tortuosity*	τ	1.65	particle zeta potential*	ψ_o	38 mV
wall zeta potential*	ψ_w	135 mV	effective diffusion coeff*	D_{eff}	$3.6 \times 10^{-9} \text{ m}^2/\text{s}$
permittivity*	ϵ_w	$51 \epsilon_o$	electric field	E_z	49200 V/m
particle diameter	dp	41 μm	fluid density*	ρ_w	836.77 kg/m ³ [2]
pore shape factor*	k_o	2	kinematic viscosity	η	$8.9 \times 10^{-7} \text{ m}^2/\text{s}$

Table 5.3: Values used to match the data from Figure 7b of Tallarek [3], using the averaged porosity variation 5.6. Values with an asterisk are estimated.

The results using the values from Table 5.3 are shown in Figure 5.9 using a constant porosity $\epsilon(r) = 0.39$, and in Figure 5.10 using equation 5.6 for the average porosity variation. It can be seen that if the porosity variation is not taken into consideration, the zeta potential mismatch does not produce the same shape as seen in the experimental data (Figure 5.9). However, the model matches the experimental data quite well, using the same parameters, if the porosity variation is taken into consideration (Figure 5.10). A wall zeta potential of -135 mV and a particle zeta potential of -38 mV was used. The diffusion coefficient of $3.6 \times 10^{-9} \text{ m}^2/\text{s}$ is only slightly higher than the effective diffusion coefficient of $3.5 \times 10^{-9} \text{ m}^2/\text{s}$ estimated by Tallarek et al [3].

Figure 5.11: Comparison of the experimental data taken from Figure 5 of Tallarek [3] with the numerical model using equation 5.6 for the average porosity variation and equations 5.15 and 5.16 for the concentration profile. The values $\psi_w = 140$ mV, $\psi_o = 34$ mV, $D_{eff} = 3.5 \times 10^{-9}$ m²/s, and $\tau = 1.65$ were used.

Variable	Symbol	Value	Variable	Symbol	Value
porosity (center)*	ϵ_o	0.4	buffer conc	C	0.002 M
tortuosity*	τ	1.65	particle zeta potential*	ψ_o	-34 mV
wall zeta potential*	ψ_w	-140 mV	effective diffusion coeff*	D_{eff}	3.5×10^{-9} m ² /s
permittivity*	ϵ_w	$51 \epsilon_o$	electric field	E_z	47400 V/m
particle diameter	dp	41 μ m	fluid density*	ρ_w	836.77 kg/m ³ [2]
pore shape factor*	k_o	2	kinematic viscosity	η	8.9×10^{-7} m ² /s

Table 5.4: Values used to match the data from Figure 5 of Tallarek [3], using the averaged porosity variation 5.6. Values with an asterisk are estimated.

The data from Figure 5 of Tallarek et al [3] was also compared with the model results, using the parameters given in Table 5.4. It was assumed that the same column was used for the experiments as in Tallarek's Figure 7b. However, a different buffer concentration was used (2 mM instead of 1 mM), implying that the zeta potentials will be slightly different. In addition, a slightly lower electric field was applied (47400 kV/m instead of 49200 kV/m), which would result in a lower temperature, and thus other parameters, such as the viscosity and the diffusion coefficient, could be impacted as well. The images for the two different experiments were taken at different times as well (120 ms for the Figure 7b data, and 40 ms for the Figure 5 data), and thus the

dispersion produced by the zeta potential mismatches is expected to be less severe in the Figure 5 results. The best fit was found manually using a wall zeta potential of -140 mV , a particle zeta potential of -34 mV , and a slightly lower diffusion coefficient of $3.5 \times 10^{-9}\text{ m}^2/\text{s}$. The results are shown in Figure 5.11. It can be seen that the models for both experiments yield similar results, although the zeta potentials are slightly different. Some of the difference may be due to the increase in buffer concentration and decrease in electric field, as previously mentioned, as well as the fact that the porosity variation has only been estimated with equation 5.6. This equation removes the effects of the oscillations in porosity, which would affect the shape of the concentration profile. It is also likely that radial diffusion across flow lines would smear out the velocity profile near the channel wall, an effect which has not been taken into consideration in this model. Still, the close agreement of theory to experimental results is encouraging. The zeta potential estimates are both within 5 mV of each other, which is a small error in this case, considering the number of variables involved.

Incorporating Radial Diffusion and Porosity Oscillations into the Model

This model was improved upon by taking into account both radial diffusion as well as the radial variations of porosity. The porosity variation from the experimental data found in Tallarek [4] and shown in Figure 5.4(a) was used, as the column-to-particle diameter ratios are nearly the same. The Brinkman equation was solved in the same way as above, but in this case the convection-diffusion equation (5.14) was solved numerically in Femlab. In order to do this, the one-dimensional flow profile determined from the Brinkman model was interpolated for use in the mesh of the two-dimensional axisymmetric convection-diffusion model. The column was $305\mu\text{m}$ long and had a radius of $125\mu\text{m}$. The region comprising the first $5\mu\text{m}$ of the channel length was assigned an initial (arbitrary) concentration of $1 \times 10^{-3}\text{ M}$. Defining a region smaller than this led to difficulties in resolving the concentration profile with the mesh, while defining regions that were larger did not have a large impact on the results, provided it did not become so large as to become comparable to the final width of the concentration profile (as for example in Figures 5.10 and 5.11). A mesh size of $1\mu\text{m}$ was assigned at the column wall, with a mesh growth rate of 1.3, for a

total number of approximately 6500 elements. To account for the fact that longitudinal dispersion is expected to be larger than transverse dispersion, an asymmetric diffusion tensor was used for the diffusion coefficient, with D_{m_r} in the radial direction and D_{m_l} in the longitudinal direction.

Figure 5.12: Comparison of the experimental data taken from Figure 7b of Tallarek [3] with the numerical model using the experimental data from Figure 5.4(a) for the porosity. The concentration profile was determined numerically. The values used for the numerical model included $\psi_w = 162$ mV, $\psi_o = 39$ mV, $D_{m_t} = 0.1 \times 10^{-9} \text{ m}^2/\text{s}$, $D_{m_l} = 5.9 \times 10^{-9} \text{ m}^2/\text{s}$, and $\tau = 1.65$. All other variables are as in Table 5.3.

It was found that including a radial diffusion component had a significant impact on the concentration curve; as expected, radial diffusion across streamlines tended to smooth out the effects of the high velocities at the column wall. Thus, a larger value of ψ_w was required in order to match the concentration profile from Figure 7b of Tallarek [3] (see Figure 5.12, $C = 1 \text{ mM}$, $E_z = 49200 \text{ kV/m}$, $t = 120 \text{ ms}$). Increasing D_{m_r} had the effect of transferring fluid in the leading edge of the distribution towards the center of the distribution, causing a large hump to appear in the concentration profile if the constant was raised too high. It was found that values of 0.1×10^{-9} and $5.9 \times 10^{-9} \text{ m}^2/\text{s}$ were required for D_{m_r} and D_{m_l} , respectively. It should be noted that $D_{m_l}/\tau = 3.57 \times 10^{-9} \text{ m}^2/\text{s}$, which is similar to the apparent diffusion coefficient estimated by Tallarek as well as that used for the analytical solution to the

convection-diffusion equation. It is accepted in the literature, both experimentally and theoretically, that there is typically an order of magnitude difference between the transverse and longitudinal dispersion coefficients [58, 12] in pressure-driven flow ($D_{m_l} \gg D_{m_r}$). Although it might be expected that the difference between the dispersion coefficients for electroosmotic flow would be less severe (based upon the dispersion theory of Section 3.3.2), the experimental data of Tallarek [4] implied that there was an order of magnitude difference in the radial and longitudinal dispersion coefficients for electroosmotic flow as well. Models of fluid flow in porous media have suggested that there is little transverse transfer of momentum in porous media [27], which suggests that the difference between dispersion coefficients might be a general characteristic of flow in porous media.

Figure 5.13: Comparison of the experimental data taken from Figure 5 of Tallarek [3] with the numerical model using the experimental data from Figure 5.4(a) for the porosity. The concentration profile was determined numerically. The values used for the numerical model included $\psi_w = 185$ mV, $\psi_o = 39$ mV, $D_{m_t} = 0.1 \times 10^{-9} \text{ m}^2/\text{s}$, $D_{m_l} = 5.9 \times 10^{-9} \text{ m}^2/\text{s}$, and $\tau = 1.65$. All other variables are as in Table 5.4.

Attempts to match the curve of Figure 5 from Tallarek [3] found the same trend for the diffusion coefficients, but a much larger zeta potential was required (see Figure 5.13, $C = 2\text{mM}$, $E_z = 47400\text{kV/m}$, $t = 40\text{ms}$). The difference between the ψ_w values for the two experiments is quite large, and suggests that there are other effects

present that are not being captured by the present model. One such effect would be that the tortuosity is typically a function of porosity [33], and, thus, the tortuosity should in reality also approach unity near the column wall. This would impact both the velocity and the effective diffusion coefficient near the wall. Dispersion could also be caused by temperature gradients in the capillary, which would affect the local flow velocity due to convection effects, changes in viscosity, and changes in the fluid density.

In addition, it is possible that pressure-gradients exist near the capillary wall, due to porosity variations (which may not be captured with this model) or thermal effects. In the experimental setup employed by Tallarek et al [3], the packed segment (with an inner diameter of 250 μm and a length of 200 mm) was followed by an open tube segment (with an inner diameter of 150 μm and a length of 200 mm). Due to the lower fluidic resistance in the open column, an intersegmental pressure will develop inside the column that will counteract the EOF [22]. The effect of the open segment of the column has been neglected here, as the effect of the intersegmental pressure on the fluid velocity in the packed segment is usually negligible in CEC columns [22]. However, the use of a one-dimensional Darcy model (as in Section 4.1) to find the intersegmental pressure (neglecting porosity variation and the higher zeta potential of wall of the packed segment) results in

$$P_{is} = - \frac{\left[\frac{A_2 \epsilon_w \psi_w \nabla \phi}{\mu_2} - \frac{A_1 K \rho_{eff} \nabla \phi}{\sqrt{\tau} \mu_1} \right]}{\frac{A_1 K}{\sqrt{\tau} \mu_1 L_1} + \frac{A_2 R_2^2}{8 \mu_2 L_2}}. \quad (5.17)$$

In this model, the zeta potential of the wall of the open segment was assumed to be ψ_w , and the cross-sectional area and length for the packed and open segment were designated by A_1, A_2 and L_1, L_2 , respectively. Using this model, the intersegmental pressure was found to be 1180 P_a . Using equation 3.1 to compare the relative importance of the electroosmotic force to the pressure force, it was found that the pressure force accounted for a reduction of 6.55% of the fluid velocity in the packed segment. This pressure force would have the largest impact on the fluid velocity near the channel walls, due to the increase in porosity in that region. The intersegmental pressure should therefore be taken into consideration in future models.

Another effect that has not been taken into consideration is the possibility of a time-dependent dispersion coefficient. Investigations performed by Tallarek et al [4] in a similar column (packed with spheres of different size) indicated that the longitudinal dispersion coefficient grew in time, eventually reaching an asymptotic value over ten times larger than the molecular diffusion coefficient [4]. The time scale required to reach the asymptotic limit was several times longer than the time frame for the experiments that are modelled here. This suggests that the apparent dispersion coefficient grows quickly over the time period of these experiments, which could help explain the need for such a high ψ_w in Figure 5.13. A time-dependent dispersion effect of this magnitude is not predicted by the models for dispersion in porous media for electroosmotic flow developed in Section 3.3, as the κa ratios in this case are quite large. The growth in dispersion is likely largely due to the porosity variations and the zeta potential mismatch, but other effects are quite possibly at play as well.

Some insight into this discrepancy can be gained by considering Tallarek et al's experimental data for dispersion in pressure-driven flow in chromatography columns [4]. The growth of dispersion over time for both electroosmotic and pressure-driven flow had the same qualitative shape, but the dispersion in pressure-driven flow was a little larger than that seen in electroosmotic flow. The theoretical models for dispersion in porous media in Section 3.3 suggested that the dispersion due to the velocity profile in individual pores and a distribution of pore sizes is negligible in electroosmotic flow (for these κa ratios), but not necessarily in pressure-driven flow.

In order to determine how the dispersion theory developed in Section 3.3 compares with the experimental data for pressure-driven flow, the particle-size distribution data from Tallarek's 41 μm experiments [3] were used to estimate the particle size distribution for the 50 μm particles used for the dispersion experiments [4]. The particle size distribution was fitted with a Gaussian curve, as shown in Figure 5.14. The standard deviation was found to be $0.214 d_p$ and the apparent maximum particle size was $1.5 d_p$. This was used to calculate the pore size distribution for the 50 μm particles, using a porosity of 0.4. Using equation 3.83 for the growth of the dispersion coefficient over time, and a correlation length of $L_h = 2M = 22.22\mu m$, the effective dispersion due to the pore size distribution was determined.

Figure 5.14: Best Gaussian fit to the distribution of particles sizes used in Tallarek's experiment [3]. The mean value is $d_p = 42\mu m$, the standard deviation is $9\mu m$ ($0.214 d_p$), and the apparent maximum particle size is $63\mu m$ ($1.5 d_p$).

Figure 5.15: Experimental dispersion values seen by Tallarek in an earlier experiment with $d_p = 50\mu m$ [4] for pressure-driven and electroosmotic flow. The theoretical dispersion curve for D_h using equation 3.83 is also shown for comparison. The mean solid particle diameter was $d_p = 50\mu m$. The mean pore size $M = 11.11\mu m$ was calculated using $\epsilon = 0.4$. The values $\sigma_a = 2.378\mu m$, and $a_{max} = 16.66\mu m$ were inferred from Figure 5.14. L_h was assumed to be $2M$.

The result can be seen in Figure 5.15, where the experimental dispersion data are illustrated, along with the calculated dispersion curves. It is apparent that the dispersion predicted using the theory from Section 3.3.2 underestimates the dispersion seen in the chromatography column. This implies that there are sources of dispersion at work other than that due to a distribution of pore sizes (such as dispersion from the porosity variations, thermal effects, zeta potential mismatches, or other, unknown, sources). However, it was found that the *difference* between the dispersion curves for pressure-driven and electroosmotic flow corresponded very well with the dispersion curve calculated using equation 3.83. This suggests that the additional sources of dispersion act equally upon both pressure-driven and the electroosmotic flow (and that the difference between the two can be associated with dispersion due to the distribution of pore sizes). It also suggests that equation 3.83 is capable of estimating the dispersion due to the heterogeneity of the medium. Thus, the growth of the dispersion coefficient over time could be partly responsible for the difference in zeta potentials seen in the numerical results.

These results imply that there is still a great deal of research that needs to be conducted on dispersion in porous media in general, and in electroosmotic flow in particular. The model for electroosmotic flow developed here can be used to match the concentration profiles seen in capillary electrochromatography; however, due to the nonlinearity of the problem and the number of variables concerned, it is possible to find more than one set of parameters that could explain the results. In addition, the zeta potentials found for the wall potential are rather high. Again, time-dependent dispersion effects could partly explain this discrepancy. It is also quite possible that temperature effects in the capillary could be partly responsible for the apparent need for large zeta potentials. The temperature in the capillary can be expected to have a roughly parabolic profile [21]. In spite of the limitations of the model, it is believed that it is a first step in understanding some of the underlying physics behind the evolution of the concentration profiles in capillary electrochromatography. However, it must also be noted that, as the generalized porous medium equation is a volume-averaged model, it will be difficult in practice to precisely match the concentration profiles of an individual experiment.

5.3 Experimental Results Using Nitrocellulose Membranes

Some very simple microfluidic circuits were built and tested, with the assistance of the microfluidics device research company Epocal, in order to demonstrate how the theory developed in this work could be used in the design of microfluidic chips. Nitrocellulose membranes were used as the porous material, and placed upon a substrate of FR-4 epoxy with gold-plated copper electrodes. The nitrocellulose membranes, obtained from Millipore Inc., were intended for filtration applications, and thus the pore size was quoted in terms of the membrane's maximum pore diameter. A silicone adhesive was used to glue the porous material to the substrate, and mylar was used to encapsulate the porous material. An air gap with a width on the order of $100\ \mu\text{m}$ was inserted between the wedge-shaped pump and the load to act as a diffusion stop. The air gap was constructed in such a way so that the air could be forced upwards into a small region above the gap, permitting the fluid to flow through unimpeded once flow was initiated.

Although a number of devices were built, only two devices were successfully tested, due to electrochemical problems with the dye and mechanical problems with its injection. The different devices used roughly the same geometry and material for the electroosmotic pump (the wedge), but used different membranes and geometries for the load region (the bottom channel). The original intent was to explore the effects of different macroscopic Peclet numbers (see Section 3.3.1) on the flow profile in the bottom channel; unfortunately, as only two different devices were tested, such effects could not be explored in detail.

Device 1

In the first device, a nitrocellulose membrane with a maximum pore size of $220\ \text{nm}$ was chosen. The porosity of the membrane was listed as 0.75, and had a thickness of $180\ \mu\text{m}$. The device shown conceptually in Figure 5.16 was built by cutting the membranes to the desired lengths. The air gap had a width of $100\ \mu\text{m}$. The bottom channel for this device was very large, and thus, with the small pore size, presented

a very large fluidic resistance to the electroosmotic pump. Very small fluid velocities can therefore be expected from this device.

Figure 5.16: Geometry of the nitrocellulose microfluidic circuit. The electrodes were spaced 4.5 mm apart. A potential of 40 V was applied to the top electrode. The pump is considered to be the region between the electrodes.

The dye (Allura Red, from Sigma-Aldrich) used in the experiments was charged; therefore, it was not possible to place it between the electrodes, because electrophoretic effects would complicate the interpretation of the results. In addition, it was found that the dye would change direction once it came near the negative electrode, implying that unwanted electrochemical effects between the dye and the buffer at the negative electrode were present. For this reason, the experiments conducted had to investigate the electroosmotic flow component indirectly, by watching the dye movement in the load regions, driven by an electroosmotic pump.

Figure 5.17: Image of the device before the application of the electric field.

A drop of 2mM concentration diethanolamine (pH 10.1) buffer was placed at the top of the wedge, and time was given for the membranes to soak up the fluid. A drop of red dye was placed at the left outlet of the load, and was allowed to diffuse through the load membrane. The diffusion gap of 0.1 mm at $y = 0$ was used to prevent the dye from spreading beyond the bottom channel. A potential of 40 V was applied to the top electrode, while the bottom electrode was grounded. A video camera attached to a microscope (Sensor Technologies America, STA-630) was used to record the movement of the dye on a VHS tape, which was later transferred to a PC for further analysis. An image of the device (prior to the application of the electric field) is illustrated in Figure 5.17.

An approximation of the fluid flow was found using the one-dimensional Darcy models of Section 4.1. As the nitrocellulose membranes were assumed to have a truncated lognormal pore size distribution, the theory from Section 3.3.2 was used to determine the permeability. The results of this model suggested that the flow speeds were very small (ranging from $\sim 100\mu\text{m}/\text{s}$ at the outlet of the wedge, to $\sim 5\mu\text{m}/\text{s}$ in the bottom channel). Thus, the nonlinear terms in the generalized porous medium equation could be neglected. The Darcy number D_a in this case was also very small, so that, technically, the viscous term was negligible as well. However, for technical reasons, the Brinkman equation was found to be more convenient, as it was difficult to develop a flexible formulation of Darcy's Law with electroosmotic forces in Femlab. A no-slip condition was applied at all walls except the inlet and outlets, although the use of a slip condition did not seem to affect the results. It was assumed that the pressure at all the inlets and outlets was zero (the drops of fluid at the top inlet and the left outlet were neglected). Although in theory the generalized porous medium could be used to model the fluid flow through the open region (the air gap), due to its small size, it was neglected, as, due to memory limitations, it was not possible to create a mesh dense enough to achieve a reasonable solution. The simulations were performed on a 2.8 GHz Pentium 4 processor running Windows 2000, with 2 Gb of RAM.

Due to the small pore size and slow fluid velocity, the pore-scale Peclet number, as well as the correlation length, L_h , were very small, and thus dispersion was neglected. The load region at the bottom of the device was assumed to have an initial

(arbitrary) concentration of $2 \times 10^{-3}M$. The convection-diffusion equation scaled by the porosity and tortuosity of the medium (5.14) was used to model the movement of the dye over time. To simplify the electrostatics model, the medium was assumed to be nonconducting, and the boundaries of the device were assumed to be perfect insulators. This allowed the permittivity of the solid portion of the porous medium to be neglected (as the electroosmotic force will be proportional to the permittivity of the fluid in any case). The Laplace equation could then be solved to find the electric field. These assumptions are not expected to have a large impact on the results; a slight change in the magnitude of the electric field should only affect the interpretation of the zeta potential for the electroosmotic pump. Alternative models that could account for the permittivity and conductivity of the solid material are discussed in the Conclusion (Chapter 6). The flow was assumed to be at steady state throughout the experiment, due to the very small time constants seen in porous media (see Section 4.3). Streaming potential effects in the load were neglected to simplify the model; however, because of the small pore size, streaming potential effects will be significant, and could account for a reduction in the flow velocity in the load region by as much as 30%. As neglecting the streaming potential effects would only be expected to impact the predicted zeta potential values, it was decided that its inclusion did not justify the added complexity to the model.

The effective charge density and the permeability in the region between the electrodes was calculated using equations 3.76 and 3.77, respectively, while the permeability outside the electrodes was calculated using equation 3.72. The pore size distribution was assumed to be a truncated lognormal distribution, and thus equations 3.69 and 3.82 were used to calculate the probability distributions. For the one-dimensional Darcy model, equation 4.18 was used to find the total resistance of the wedge. Equations 4.19 and 4.22 were solved to find the flow in each arm of the T intersection. The results of the one-dimensional Darcy model and the numerical results are compared in Table 5.5. The macroscopic Peclet number ($\bar{u}W/D$) in the load region was found to be between 124 and 144. The critical length required in the load region (for which variations in concentration could be expected to decrease to 37% of their initial value), using equation 3.61, was estimated to be between 0.143 and 0.166 m , plus the length

of the region required for the velocity to reach a constant value away from the inter-section. It can be seen, then, that the concentration profile cannot be expected to smooth out considerably, prior to leaving the load region, using this device.

Variable	Value	Variable	Value	%Difference
$\bar{u}_{D_{wo}}$	$112.91 \mu m/s$	$\bar{u}_{FEM_{wo}}$	$74.291 \mu m/s$	34.20%
$\bar{u}_{D_{lo}}$	$10.1 \mu m/s$	$\bar{u}_{FEM_{lo}}$	$7.69 \mu m/s$	24.10%
$\bar{u}_{D_{ro}}$	$8.72 \mu m/s$	$\bar{u}_{FEM_{ro}}$	$6.63 \mu m/s$	24.0%
$U_{D_{wi}}$	$1.073 \times 10^{-7} m^2/s$	$U_{FEM_{wi}}$	$0.852 \times 10^{-7} m^2/s$	20.6%
$U_{D_{lo}}$	$0.576 \times 10^{-7} m^2/s$	$U_{FEM_{lo}}$	$0.434 \times 10^{-7} m^2/s$	24.6%
$U_{D_{ro}}$	$0.497 \times 10^{-7} m^2/s$	$U_{FEM_{ro}}$	$0.375 \times 10^{-7} m^2/s$	24.6%
$U_{D_{wi}} - \sum U_{D_o}$	$0 m^2/s$	$U_{FEM_{wi}} - \sum U_{FEM_o}$	$0.04 \times 10^{-7} m^2/s$	

Table 5.5: Comparison of the one-dimensional Darcy model and the numerical results for Device 1. The parameters used are the same as those given in Figure 5.19. $\bar{u}_{D_{wo}}$ and $\bar{u}_{FEM_{wo}}$ refer to the Darcy and numerical velocity at the outlet of the wedge. The subscript *lo* refers to the left outlet, *ro* refers to the right outlet, and *wi* refers to the wedge inlet. U denotes the 2D volume flow in m^2/s . The difference between the inlet and outlet volume flows is denoted $U_{D_{wi}} - \sum U_{D_o}$.

It can be seen from the results in Table 5.5 that the Darcy model and the numerical model show significant differences in their flow predictions; this is believed to be due largely to the calculation of the pressure in the one-dimensional Darcy model using equation 4.22. The pressure was calculated using the Darcy model as 122690 Pa , but in the numerical model it reaches a maximum value of 308400 Pa at the ground electrode, and is reduced to 181000 Pa at the wedge outlet. It can be seen that the one-dimensional model over-predicts the flow velocity by as much as 35 %. An estimate of the error in the numerical model can be obtained by finding the difference between the total volume flow at the inlet versus the outlets. The difference of $0.04 \times 10^{-7} m^2/s$ corresponds to an error of 4.69 % relative to the volume flow at the wedge inlet.

In order to facilitate the comparison of the numerical and experimental results, the bottom channel in the images of the dye at different times were imported into Femlab. Three contour levels from the numerical solution were then superimposed upon the experimental results (representing the 80%, 85%, and 90% concentration levels). These contour levels were intended to represent the approximate threshold of dye visibility in the digitized images. A sample solution of the numerical model without the experimental data is shown in Figure 5.18.

A maximum mesh size of 0.3 mm was used in all segments of the device, with the

Figure 5.18: Example of the predicted concentration profile, without the superposition of the experimental results (at $t = 244.26$ seconds).

exception of the portion between the negative electrode and the bottom channel, which had a maximum mesh size of 0.1 mm. The resulting mesh had a total of 6353 elements. Because many of the parameters, such as the zeta potential, the buffer permittivity, the diffusion coefficient of the dye, the shape of the pore size distribution, or the tortuosity, are unknown, there is likely more than one possible set of parameters that could be used to fit the model to the data. One possible solution sequence is shown in Figure 5.19. The small diffusion coefficient of $0.2 \times 10^{-9} \text{ m}^2/\text{s}$ is in the range of that found for other dyes [72]. The arrows in the figures indicate the direction of fluid flow, and their size is proportional to the volume-averaged velocity.

It can be seen from the figures that the model can only capture the experimental results in a general sense. There appears to be a region of higher permeability near the walls of the bottom channel, and it can be seen that the model underestimates the distance the dye has travelled in the horizontal directions. It is quite possible that the nitrocellulose membrane has an anisotropic permeability, which could result in an asymmetry such as that seen here. Another possibility is a scaling error in the experimental results images or in the measurement of the device dimensions. A small scaling error (stretching or shrinking the image) could significantly impact the results, as the fluid velocity decays exponentially away from the electroosmotic pump. The velocity profile along a vertical cross-section down the center of the device (at

Figure 5.19: Matching of predicted contours to the experimental data for Device 1, using $D_m = 0.2 \times 10^{-9} \text{m}^2/\text{s}$. The contours represent the 80%, 85%, and 90% concentration levels. The values $\psi_o = -30\text{mV}$, $\epsilon = 0.75$, $\tau = 1.4$, $M = 85\text{nm}$, $\sigma_a = 18\text{nm}$, $a_{max} = 110\text{nm}$, $\epsilon_w = 51\epsilon_o$, $\rho_w = 836.77\text{kg}/\text{m}^3$, $\eta = 8.9 \times 10^{-7} \text{m}^2/\text{s}$, $1/\kappa = 3 \text{nm}$, and $D_m = 0.2 \times 10^{-9} \text{m}^2/\text{s}$ were used. The lighter regions in the imported image have higher concentration. The dark region on the right was outside of the camera viewpoint.

$x = 0$) is shown in Figure 5.20. It can be seen that, due to the nonlinear nature of the velocity profile, a small linear scaling or measurement error in the x or y coordinates would result in a nonlinear scaling of the dye movement over time.

Figure 5.20: Velocity profile along a cross-section down the center of the device ($x = 0$). The bottom channel is located at $y < 0$.

The experimental results also seemed to demonstrate a reduction in flow rate over time. For the larger times (Figure 5.19, at $t = 244.26s$), it can be seen that the predicted dye profile has moved faster in both the vertical and horizontal directions than the experimental dye profile. The reduction in velocity could be due to the formation of bubbles (due to the electrolysis of water), due to polarization of the electrodes, or possibly due to a change in the pH (and hence the zeta potential of the membranes).

These factors were taken into consideration using a more complex model, in which the permeability in the horizontal direction in the bottom channel was assumed to be twice that in the vertical direction. In addition, the applied voltage at the electrodes was assumed to decay exponentially in time using an empirical equation,

$$\phi(t) = 40(1 - 2.6 \times 10^{-3}t)e^{\frac{-t}{150}}. \quad (5.18)$$

This equation is plotted in Figure 5.21. The form of this equation was found by solving the numerical model numerous times in order to determine the apparent decay in potential over time. In each case, the concentration contours were matched with

Figure 5.21: Applied voltage over time, using equation 5.18.

the experimental profiles at a different time. Once again, this was complicated by the fact that the velocity decreases exponentially away from the electroosmotic pump, and thus equation 5.18 had to be modified empirically. The model was solved again, using the final form of equation 5.18 for the applied potential at the top electrode. The results for the simulation are shown in Figure 5.22. It can be seen that a much better match with the data is obtained with this model. The contours predicted by the numerical model are in much better agreement with the experimental profiles.

Figure 5.22: Matching of predicted contours to the experimental data for Device 1, using $D_m = 2.2 \times 10^{-9} \text{m}^2/\text{s}$, $K_x = 2K_y$, and equation 5.18 for $\phi(t)$. The contours represent the 80%, 85%, and 90% concentration levels. The values $\psi_o = -38\text{mV}$, $\epsilon = 0.75$, $\tau = 1.4$, $M = 75\text{nm}$, $\sigma_a = 15\text{nm}$, $a_{\max} = 110\text{nm}$, $\epsilon_w = 60\epsilon_o$, $\rho_w = 836.77\text{kg}/\text{m}^3$, $\eta = 8.9 \times 10^{-7} \text{m}^2/\text{s}$, $1/\kappa = 3 \text{nm}$, and $D_m = 0.2 \times 10^{-9} \text{m}^2/\text{s}$ were used.

Second Device

A second device was built using a much narrower load as the bottom channel. The bottom channel also used a different nitrocellulose membrane as its porous material, with a porosity of 0.84, a listed maximum pore radius of $2.5 \mu m$, and a thickness of $160 \mu m$. The electroosmotic pump (the wedge) was built using the same material as in the first device. A conceptual illustration of the second device is shown in Figure 5.23, while an actual image of the device prior to the application of the electric field is shown in Figure 5.24. It can be seen that the device is slightly damaged at the outlet of the wedge. The bottom channel for this device much narrower than that of Device 1, and, with the larger pore size, presented a much smaller fluidic resistance to the electroosmotic pump. Significantly higher fluid velocities can therefore be expected from this device than from Device 1.

Figure 5.23: Conceptual illustration of the second device.

The use of a one-dimensional Darcy model suggested that the fluid velocity was once again small enough that the nonlinear terms could be neglected. The effective dispersion coefficient $D_{h\infty}$, calculated using equation 3.84, was reached asymptotically in around 2 seconds, and was on the order of $0.1 \times 10^{-9} m^2/s$, which is close to the diffusion coefficient of the dye. However, since the dye diffusion coefficient was so small, and was estimated only, the effects of dispersion were neglected.

The mesh employed for the numerical model used a 0.3 mm maximum element size between the electrodes, and 0.1 mm elsewhere. A potential of 40 Volts was once again applied to the top electrode. In this case, the decline in voltage over time was

Figure 5.24: Image of the second device prior to the application of the electric field.

neglected, as the time scale was much shorter than that used for Device 1. Otherwise, the numerical model was solved similarly as for Device 1. It was found that the asymmetry in the permeability for the bottom channel required to match the experimental results was $K_x = 3K_y$. Although it is not surprising to find that the permeability is asymmetric, it is also possible that a scaling error or an improper choice of material parameters for the model are also responsible for the asymmetry requirement. For example, using $M_2 = 1.8\mu m$, $\sigma_{a_2} = 500nm$, and $a_{max_2} = 2.5\mu m$ for the material parameters for the bottom channel (the mean pore size, standard deviation, and maximum pore size, respectively), the permeability can be found, using equation 3.72, to be $3.43 \times 10^{-13} m^2/s$. However, if the values were changed to $M_2 = 2.2\mu m$ and $\sigma_{a_2} = 200nm$ instead, the permeability is found to be $4.64 \times 10^{-13} m^2/s$, which corresponds to an increase in the permeability of 1.41. Thus, the asymmetry seen in permeability may simply be due to uncertainty in the data.

The numerical results are shown in Figures 5.25 and 5.26. The results suggest that there are a number of effects that have not been considered in the model. However, the numerical results are able to provide an estimate of the expected position of the dye. An estimate of the error in the numerical results can once again be found by finding the difference between the inlet and outlet flows. The velocity was found to be $188.9 \mu m/s$ at the outlet of the wedge, $132.1 \mu m/s$ at the left outlet, and $169.88 \mu m/s$ at the right outlet. The volume flows were found to be $2.315 \times 10^{-7} m^2/s$ at the wedge inlet, $0.859 \times 10^{-7} m^2/s$ at the left outlet, and $1.105 \times 10^{-7} m^2/s$ at the right outlet. This corresponds to a difference between the inlet and outlets of 0.351

Figure 5.25: Matching of predicted contours to the experimental data for Device 2, at times $t=4.02$, $t=6.12$, $t=10.41$, and $t=18.52$ seconds, using $D_m = 0.2 \times 10^{-9} \text{m}^2/\text{s}$, and $K_x = 3K_y$. The contours represent the 80%, 85%, and 90% concentration levels. The values $\psi_o = -38\text{mV}$, $\epsilon_1 = 0.75$, $\tau_1 = 1.4$, $M_1 = 75\text{nm}$, $\sigma_{a_1} = 15\text{nm}$, $a_{max_1} = 110\text{nm}$, $\epsilon_2 = 0.84$, $\tau_2 = 1.2$, $M_2 = 1.8\mu\text{m}$, $\sigma_{a_2} = 500\text{nm}$, $a_{max_2} = 2.5\mu\text{m}$, $\epsilon_w = 60\epsilon_o$, $\rho_w = 836.77\text{kg}/\text{m}^3$, $\eta = 8.9 \times 10^{-7} \text{m}^2/\text{s}$, $1/\kappa = 3 \text{nm}$, and $D_m = 0.2 \times 10^{-9} \text{m}^2/\text{s}$ were used. The subscript 1 indicates is used for values in the wedge, while the subscript 2 is used for values in the bottom region.

Figure 5.26: Matching of predicted contours to the experimental data for device 2, at time $t=35.20$ seconds, using $D_m = 0.2 \times 10^{-9} \text{ m}^2/\text{s}$, and $K_x = 3K_y$. The contours represent the 80%, 85%, and 90% concentration levels. The values $\psi_o = -38 \text{ mV}$, $\epsilon_1 = 0.75$, $\tau_1 = 1.4$, $M_1 = 75 \text{ nm}$, $\sigma_{a_1} = 15 \text{ nm}$, $a_{max_1} = 110 \text{ nm}$, $\epsilon_2 = 0.84$, $\tau_2 = 1.2$, $M_2 = 1.8 \mu\text{m}$, $\sigma_{a_2} = 500 \text{ nm}$, $a_{max_2} = 2.5 \mu\text{m}$, $\epsilon_w = 60\epsilon_o$, $\rho_w = 836.77 \text{ kg/m}^3$, $\eta = 8.9 \times 10^{-7} \text{ m}^2/\text{s}$, $1/\kappa = 3 \text{ nm}$, and $D_m = 0.2 \times 10^{-9} \text{ m}^2/\text{s}$ were used. The subscript 1 indicates is used for values in the wedge, while the subscript 2 is used for values in the bottom region.

$\times 10^{-7} \text{ m}^2/\text{s}$, which is an error of 15 % relative to the inlet, indicating that the numerical results are not as reliable as those for Device 1. The macroscopic Peclet number ($\bar{u}W/D$) in the load region was found to be between 221 and 285. The critical length required in the load region (for which variations in concentration could be expected to decrease to 37% of their initial value), using equation 3.61, was estimated to be between 0.03 and 0.039 m , plus the length of the region required for the velocity to reach a constant value away from the intersection. The concentration profile cannot be expected to smooth out considerably, prior to leaving the load region, using this device either.

These results indicate that the theory developed in this work can be used to create estimates of the expected flow and concentration profiles in microfluidic devices. However, it is also clear that many effects not considered by the model will be present in a practical device, such as thermal or electrochemical effects, bubble formation, or local regions of different permeability. The images of Device 1 revealed the presence of fingerprints on the membranes, while those of Device 2 revealed that the device

was damaged between the two membranes. Thus, it will be difficult to fit the results of any given experiment exactly. The model developed here has a very large number of input parameters, very few of which will be known to the researcher without a carefully devised research plan set up explicitly to eliminate many of the unknowns. However, it is believed that the theory developed here provides a general framework for modelling microfluidic devices incorporating porous media, permitting researchers to investigate many design parameters theoretically without the ambiguity of their experiments. This in turn would allow them to troubleshoot the design of their devices, the design of their experiments, and the theory itself.

5.4 Conclusion

In this chapter, the theory was used to fit experimental data from the chromatography literature, as well as experiments conducted in porous channels made from nitrocellulose membranes.

It was seen that the theory can be used to model flow in capillary electrochromatography channels. The Darcy formulation can be used if the ratio of the column diameter to the particle diameter is large and the zeta potentials of the different materials are equal, while the Brinkman formulation can be used if the zeta potentials are mismatched. The electrokinetic wall effect in capillary electrochromatography was investigated by taking into consideration both the porosity variation and the difference in zeta potentials near the column walls. This is the first known model to take both effects into consideration. It was found that the theory could be used to reproduce the concentration profiles observed in the literature, although the predicted column zeta potential at the wall required to match the data was rather high. This could be due to factors not considered by the model, such as tortuosity variation, temperature variation, or a time-dependent dispersion coefficient. It is also possible that, due to the small column-diameter to particle-diameter ratio (6 for the experiments of Tallarek et al [3]), the volume-averaged theory has reached the limits of applicability, and much more complicated models requiring more detailed knowledge of the pore structure might be needed to fully describe the flow profile. However, models incorporating detailed knowledge of the pore structure would be far more difficult to

implement, and require much more memory. The fact that the theory was capable of matching the flow profiles, however, suggests that the volume-averaged theory is still useful, in spite of the small ratio. The small column-diameter to particle-diameter ratio used by Tallarek et al was chosen due to resolution limits with the MRI technique employed to image the movement of the fluid. Such a small ratio will not likely be used in many practical situations.

The theory was next used to fit the concentration profiles obtained in experiments with simple microfluidic devices made with nitrocellulose membranes. It was found that the theory could be used to fit the data, although there were many unknowns in the experiments, making it difficult to draw firm conclusions. The experimental results suggested that electrochemical effects were present, and that the permeability of the porous material was anisotropic. These assumptions can only be confirmed through additional experiments. The experiments, therefore, illustrated the utility of the model for the design of microfluidic circuits, but at the same time highlighted some of its deficiencies, due to effects that have yet to be incorporated into the model. More realistic models will need to take into consideration thermal effects, electrochemical effects, and anisotropic quantities in order to be able to make more accurate predictions.

Chapter 6

Conclusion

6.1 Summary of Results and Contributions

In this work, the standard model for electroosmotic flow in porous media was extended so as to incorporate viscous effects near solid boundaries, as well as nonlinear effects at higher flow rates. Although the use of a viscous term has been suggested in the chromatography literature [23], this is the first known formulation to include both effects. The model has been based upon the generalized porous medium equations for pressure-driven flow in porous media [6, 7, 27], and thus results in a flexible model that is applicable over a wide range of flow conditions, in open channels as well as in porous media. The formulation differs from the pressure-driven flow models in the literature in that the tortuosity has been incorporated explicitly into the model.

The electroosmotic force term has been incorporated using an effective charge density that results in the same volume flow in a single pore as the actual charge density, but is independent of position in the pore. This formulation was shown to reproduce the basic models for electroosmotic flow in the literature. Although this model has neglected effects such as, for example, polarization of the double layer, axial changes in zeta potential, or gradients in buffer concentration, it should be possible to incorporate such effects into the model for the effective charge density by redefining the total volume flow in a single pore due to an applied electric field (see equation 3.3).

The generalized porous medium equation was found to be governed by three different dimensionless numbers, which could be used to determine when different terms in the equation become important. It was found that the generalized porous medium

equation is equivalent to the Forchheimer equation at high flow speeds, the Brinkman equation when viscous effects become significant, and Darcy's Law when the Darcy number is very small. In addition, the equation reduces to the Navier-Stokes equations when the porosity and the tortuosity of the medium approach unity, allowing both porous and open channels to be modelled simultaneously. This flexibility permits modelling of both pressure-driven and electroosmotic flow in a wide range of possible scenarios.

Models for dispersion for pressure-driven flow were then adapted for use in electroosmotic flow. Taylor's approach for dispersion in a tube was applied to electroosmotic flow, resulting in an effective dispersion coefficient that is dependent upon the double layer thickness and the Peclet number. This result was found to be consistent with that of a different analysis in the literature [10]. It was found that dispersion due to the velocity profile in an individual pore can usually be neglected.

Stochastic models for groundwater flow from the literature were then used to develop expressions for the effective permeability and effective charge density of a heterogeneous porous medium. Using these models, an effective dispersion coefficient that is dependent upon time was obtained. By neglecting the effects of transverse diffusion, breakthrough curves were plotted for both pressure-driven and electroosmotic flow. This is the first known model that can predict breakthrough curves for electroosmotic flow in heterogeneous porous media. These curves indicated that very little dispersion will occur in electroosmotic flow if the majority of the pore size distribution is much larger than the double layer thickness. Although the model predicted significant dispersion if the pore size distribution included a large number of pores on the order of the double layer thickness, it was found that if transverse diffusion was taken into consideration, diffusion across streamlines would significantly reduce the amount of dispersion seen by an analyte. Thus, it was seen that dispersion in electroosmotic flow in heterogeneous media can usually be neglected. This model represents the first known model of dispersion due to a distribution of pore sizes in electroosmotic flow.

The generalized porous medium equation was then used in Chapter 4 to find analytical expressions for fluid flow in a number of different geometries. In most cases,

the Darcy model was applicable, and thus one-dimensional models for fluid flow in a variety of different geometries were developed. This permitted simple investigations of different configurations of electroosmotic pumps (defined as the region between the electrodes) and loads. Although the one-dimensional theory was able to accurately predict the flow velocity in a variety of channels, it could not capture the variation in velocity near boundaries, or the variation in pressure near intersections. In such cases, a numerical model or more sophisticated analytical techniques (such as the use of complex analysis in the case of relatively simple geometries) would be required. Some examples of complex analysis and conformal mappings applied to porous media flow (Darcy flow) are reviewed in the book by Bear [73].

Analytical solutions to the Brinkman equation were then found for flow in a number of simple geometries with uncharged walls. It was found that the flow velocity went to zero in a small region close to the wall proportional to the square root of the permeability. Channels with charged walls were then considered, in which the zeta potential of the porous material did not match that of the walls. It was found that the drag induced by the porous medium ensured that the increase in fluid velocity was confined to a small boundary region near the wall. This model was further refined to include the effects of a step increase in porosity near the wall. It was seen that this could significantly affect the thickness of the boundary region, as well as the volume flow near the wall. This is the first known model to take both the effects of porosity variation and a zeta potential mismatch into consideration, and could be useful, for example, in models for capillary electrochromatography, where both these effects are important.

In Chapter 5, the theory was used to fit the experimental results seen in the capillary electrochromatography literature. It was found that the theory was able to fit the flow velocity data presented by Liapis and Grimes [2], using the same parameters as in their model. This indicates that the Darcy formulation of the generalized porous medium equation is equivalent to the model developed by Liapis and Grimes. The theory was then used to model the flow through the porous particles, and the predictions were similar to those given by a network model used by Liapis and Grimes [71].

The Brinkman formulation of the generalized porous medium equation was then used to model wall effects in capillary electrochromatography. It was found that a very good match between theory and the experimental results of Tallarek et al [3] could be found if the effects of transverse diffusion were neglected. If the effects of transverse diffusion were taken into consideration, it was found that the diffusion coefficients required to fit the data were at least an order of magnitude apart, a situation that has been found to be true experimentally [4]. However, the column zeta potentials required to fit the data were quite large, and a large difference was found between the column zeta potentials of two different experiments. This suggests that there are other effects present that have not been included in the model, such as variations in tortuosity near the wall, thermal effects, and a dispersion coefficient that is dependent on time. Such effects could be incorporated into the present model, although they are beyond the scope of the present work. This is the first known attempt to fit experimental concentration profiles for electroosmotic flow with a theoretical model.

Finally, two simple microfluidic devices were obtained, which used nitrocellulose membranes as a porous material. The electroosmotic force on the fluid was inferred by watching the movement of a dye in a load region connected to an electroosmotic pump. It was found that the theory was capable of fitting the experimental results, although, due to the number of unknowns in the experiment, there are likely many alternative parameter sets that could be used to fit the data. This work represents the first known application of a theoretical model to fit experimental data from microfluidic devices employing porous materials and electroosmotic flow. The experiments highlighted many practical aspects of microfluidic devices that have not been considered using the current theory, such as electrochemical effects, anisotropic properties of the porous material, and other sources of dispersion. However, the generalized porous medium equation for electroosmotic flow derived here is expected to be a useful starting place for the design of more complicated microfluidic devices.

6.2 Future Work

There are many details that need to be investigated in future work. It should be possible to incorporate more sophisticated electroosmotic flow models into the effective charge density expression, so as to include effects such as the polarization of the double layer [44, 74], axial variations in pore radius or zeta potential [75, 76], or the adsorption of analytes onto the pore walls [40]. As mentioned earlier, convection and dispersion in porous media is still a very active area of research, and dispersion due to electroosmotic flow in porous media has received relatively little attention. The models for dispersion in this work neglected the dispersion that would occur due to pores that are randomly oriented relative to the applied pressure or potential gradient, or dispersion that would arise at junctions between different pores. A review of some of the early models for such effects in pressure-driven flow is given in the book by Bear [73]. Thermal effects in the porous material need to be taken into consideration; this has been an active research area in the past, and thus there is a wealth of material on the topic (see for example, reference [7], or the book by Nield and Bejan [27]).

The nonlinear Forchheimer term has not been applied to electroosmotic flow in porous media prior to this work; although it might be expected that the same inertial effects would occur in electroosmotic flow as in pressure-driven flow, it is possible that, due to smaller hydrodynamic boundary layers near the solid material of the porous medium, the nonlinear effects will not appear in the same fashion. As the Forchheimer equation is largely an empirical equation, this effect can only be discovered by experiment; this could prove difficult, as the high flow rates required are difficult to obtain in electroosmotic flow. Nonlinear effects are seen in electroosmotic flow at high flow rates, although these effects are normally attributed to an increase in temperature due to the high electric fields required. Thus, temperature effects could very well mask any nonlinear drag effects. It is possible that the nonlinear drag could be investigated by using highly porous media with large pore sizes, as much smaller velocities are required in this case (see Figures 3.1 and 3.2). Nonlinear drag effects could also be investigated by using a combination of pressure-driven and electroosmotic flow, as it would be easier to obtain the higher flow rates required. Fortunately, current devices typically do not need to consider the nonlinear drag effects, as they

will normally employ low flow rates.

The electromagnetic problems considered in this work have been greatly simplified by neglecting the permittivity of the solid matrix, by assuming that the solid matrix is nonconducting, and that the channel walls are perfect insulators. More realistic models would need to relax these assumptions. A number of models exist for determining the effective permittivity of a porous medium; one of the most commonly used is that of Bruggeman [67,68]. Such models will become much more important if low frequency electric fields are used, as the effective permittivity of the medium will become dependent upon the frequency of applied field, and could impact the double layer. Del Rio and Whitaker attempted to apply the theory of volume averaging to Maxwell's equations in porous media [69,70], although the conductivity of the medium and surface charge effects were neglected. They then applied their theory to fluid flow through porous media in a later article [77]. However, their results are valid only for a very limited set of conditions.

The use of low frequency electric fields has been suggested as a means for minimizing bubble formation due to electrolysis at the electrodes [20]. At higher frequencies, double layer effects near the electrodes result in polarization of the electrodes [78]. In addition, dielectrophoretic effects, in which differences between the permittivity of a particle and the surrounding fluid are employed to exert a force on the particle that is dependent upon frequency, are becoming increasingly used in microfluidic devices [79]. It is clear that a more rigorous electromagnetic treatment of the problem is becoming increasingly important.

In this work, a general framework for modelling pressure-driven and electroosmotic flow was developed that can be used to model microfluidic devices employing both open and porous channels. This will help researchers design more complicated microfluidic devices that incorporate porous material, either to enhance separations, to provide more surface area to which analytes can bind, or for use in electroosmotic pumps that are relatively insensitive to backpressure buildup. Microfluidic devices have the potential to greatly reduce the size, analysis time, and cost, of, for example, medical diagnostic devices or environmental sensors. In order to realize such

advances, it will be necessary to combine both laboratory experiments and theoretical models. The theory developed here opens up new avenues of research to help researchers achieve these goals.

Chapter 7

Appendices

7.1 List of Variables

The variables used throughout this document are listed in the table below:

Symbol	Variable	Units
A	cross-sectional area of the porous medium	m^2
A_e	effective cross-sectional area of the porous medium	m^2
A_p	cross-sectional area of a single pore	m^2
A_s	surface area of the solid phase	m^2
a	pore radius	m
β	electroosmotic coupling tensor	m^2/Vs
γ	packing parameter	
C	concentration	mol/L
D	diffusion coefficient	m^2/s
D_a	Darcy number K/L^2	
D_m	molecular diffusion coefficient	m^2/s
D_h	dispersion coeff. due to the heterogeneity of the medium	m^2/s
D_{h_P}	D_h for pressure-driven flow	m^2/s
$D_{h_{EOF}}$	D_h for electroosmotic flow	m^2/s
D_{h_∞}	asymptotic value of D_h	m^2/s
D_{eff}	effective diffusion/dispersion coefficient	m^2/s
D_{m_r}	transverse diffusion/dispersion coefficient	m^2/s
D_{m_l}	longitudinal diffusion/dispersion coefficient	m^2/s
d_p	solid particle diameter	m

d_{pp}	effective solid particle diameter of the porous particle	m
ϵ	porosity	
ϵ_p	porosity of the porous particle	
ϵ_{pe}	effective porosity of the porous particle	
ϵ_{tot}	total porosity of the column, $\epsilon + \epsilon_{pe}$	
ϵ_o	permittivity of free space	F/m
ϵ_w	permittivity of the fluid	F/m
E	externally applied electric field	V/m
e	charge of an electron	C
F_ϵ	Forchheimer drag coefficient	
G	$\nabla P + \rho_{eff} \nabla \phi$	N/m^3
g	acceleration due to gravity	m/s^2
η	kinematic viscosity	m^2/s
η_e	effective kinematic viscosity in the porous medium	m^2/s
I_n	modified Bessel function of the first kind of order n	
i	current	C/s
J_n	Bessel function of the first kind of order n	
κ	inverse debye length	$1/m$
κa	pore radius to Debye length ratio	
K	permeability	m^2
K_n	modified Bessel function of the second kind of order n	
$\overline{K}$	average permeability in a heterogeneous medium	m^2
k	Boltzmann constant	J/K
k_o	pore shape factor	
Λ	$\eta_e / (2F_\epsilon \sqrt{K})$	m/s
λ	inverse Brinkman screening length, $\sqrt{\frac{\epsilon \sqrt{\tau} \eta_e}{K \eta}}$	$1/m$
l	average length of a pore	m
L	length scale of the porous medium	m
L_h	typical length scale of the heterogeneous medium	m
μ	coefficient of viscosity	$P_a s$
μ_e	effective coefficient of viscosity in the porous medium	$P_a s$
M	mean pore radius	m
m	mean hydraulic radius	m

N	number of pores in a cross-section of the porous medium	m
n_i	bulk concentration of ionic species i	molecules/L
P	pressure	N/m^2
P_b	effective backpressure	N/m^2
P_e	Peclet number (usually defined as ua/D)	
P_{eff}	pressure force equivalent to electroosmotic force	N/m^2
$p_a(a)$	pore radius distribution	$1/m$
$p'_a(a)$	truncated pore radius distribution	$1/m$
ξ	length scale of average pore size	m
ρ	charge density distribution	C/m^3
ρ_{eff}	effective charge density of the medium	C/m^3
ρ_w	fluid density	kg/m^3
R	fluidic resistance	$P_a s/m$
R_e	modified Reynolds number	
r	radial position	m
r_s	radius of sphere	m
σ_K^2	variance of the permeability	m^4
$\sigma_{K\rho_{eff}}^2$	variance of the product of ρ_{eff} and K	C^2/m^2
σ_a^2	variance of the pore radius	m^2
σ_o	conductivity of the fluid	S/m
σ_s	surface conductivity of the solid phase	S/m
σ^*	conductivity in the porous medium	S/m
S	surface area per unit volume of the solid phase	$1/m$
τ	tortuosity	
T	temperature	K
t	time	s
u	unscaled fluid velocity	m/s
u^*	non-dimensional fluid velocity	
$\bar{u}$	volume-averaged velocity	m/s
u_{ave}	intrinsic fluid velocity in the pores	m/s
u_d	Darcy velocity	m/s
u_s	Smoluchowski velocity	m/s
U	volume flow	m^3/s

U_{ave}	average volume flow through a cross-section	m/s
ϕ	externally applied voltage	V
V_s	volume of the solid phase	m^3
x	position	m
χ	electroosmotic coupling tensor	m^2/Vs
ψ	potential distribution due to ψ_o	V
ψ_o	zeta potential of the pore surface	V
ψ_w	zeta potential of the channel wall	V
ω	ratio of the variance to the square of the mean	
z	axial position	m
z	charge number of an ionic species	

Table 7.1: Variables used throughout this document

7.2 Implementation of Ratios of Hyperbolic Functions and Modified Bessel Functions in Matlab

Due to the exponential nature of the hyperbolic functions ($\sinh(x)$, $\cosh(x)$) and the modified Bessel functions, the Matlab implementation of these functions could only be computed up to a value of approximately $x \approx 700$. However, the functional form of these equations can be rewritten in such a way that enables computation for much higher values of x . The functional forms employed for the hyperbolic functions were those suggested by Al-Hadhrani et al [66]. Similar functional forms can be employed for ratios of the modified Bessel function.

The ratio of hyperbolic cosine functions can be rewritten as

$$\frac{\cosh(x)}{\cosh(a)} = \begin{cases} e^{(x-a)} \left(\frac{1+e^{-2x}}{1+e^{-2a}} \right) & \text{if } x \geq 0, \\ e^{-(x+a)} \left(\frac{1+e^{2x}}{1+e^{2a}} \right) & \text{if } x < 0, \end{cases} \quad (7.1)$$

where it has been assumed that $x \leq a$. Expressing the ratios in this form ensures that all exponentials have negative parameters. Similarly, ratios of hyperbolic sine

functions can be expressed as

$$\frac{\sinh(x)}{\sinh(a)} = \begin{cases} e^{x-a} \left(\frac{1-e^{-2x}}{1-e^{-2a}} \right) & \text{if } x \geq 0, \\ e^{-(x+a)} \left(\frac{e^{2x}-1}{1-e^{-2a}} \right) & \text{if } x < 0., \end{cases} \quad (7.2)$$

where once again $x \leq a$.

A similar strategy can be used for ratios of modified Bessel functions. The asymptotic form for the modified Bessel function of the first kind of order zero (for $x \gg 0$) is

$$I_o(x) \approx \frac{e^x}{\sqrt{2\pi x}}. \quad (7.3)$$

Noting that $\frac{d}{dx}I_o(x) = I_1(x)$, the asymptotic form for the modified Bessel function of the first kind of order one is

$$I_1(x) \approx \left(\frac{e^x}{x\sqrt{2\pi x}} \right) \left(x - \frac{1}{2} \right). \quad (7.4)$$

Ratios such as $\frac{I_o(x)}{I_o(a)}$ were therefore calculated as (assuming once again that $x \leq a$)

$$\frac{I_o(x)}{I_o(a)} \approx \begin{cases} \frac{I_o(x)}{I_o(a)} & \text{if } x < 700 \text{ and } a < 700, \\ I_o(x)e^{-a}\sqrt{2\pi a} & \text{if } x < 700 \text{ and } a > 700, \\ e^{(x-a)}\sqrt{\frac{a}{x}} & \text{if } x > 700 \text{ and } a > 700. \end{cases} \quad (7.5)$$

Similarly, ratios such as $\frac{I_1(x)}{I_o(a)}$ were calculated as

$$\frac{I_1(x)}{I_o(a)} \approx \begin{cases} \frac{I_1(x)}{I_o(a)} & \text{if } x < 700 \text{ and } a < 700, \\ 0 & \text{if } x = 0 \text{ and } a > 700, \\ e^{(x-a)}\sqrt{\frac{a}{x}} \left(1 - \frac{1}{2x} \right) & \text{if } x > 0 \text{ and } a > 700. \end{cases} \quad (7.6)$$

These relations extend the range of computation of the above functions, and since they employ the normal definitions if the input parameters are small, they are no less accurate than the normal definitions.

7.3 Numerical Modelling Using Femlab

Femlab, a commercial software product developed by COMSOL, Inc, was used for the numerical models. This section will give some of the details needed to implement some of the models used in this work in Femlab. The models were developed in both Femlab 2.3 and Femlab 3.0. The models were usually exported to Matlab (a commercial software product developed by Mathworks, Inc) and run as m-files.

Typically, three application modes were needed to solve the numerical models. One application mode was required for the electromagnetic or the charge distribution problem, one was required for the fluid flow problem, and a third was required for the convection-diffusion problem. The models would typically be solved in that order, i.e. the electromagnetic problem would be solved first, followed by the fluid flow problem, and the convection-diffusion problem would be solved last.

The Poisson-Boltzmann equation (2.55) was typically solved using a one-dimensional axisymmetric application mode, such as the Heat Transfer application mode (which had the form of Poisson's equation). If the Brinkman equation was to be solved using a one-dimensional axisymmetric model as well, the Heat Transfer application mode was used for it as well. For example, the models used to fit the experimental data of Tallarek et al presented in Section 5.2.4 used the one-dimensional axisymmetric Heat Transfer application mode three different times; once for the ψ_w contribution to the charge distribution, once for the ψ_o contribution, and once for the fluid flow problem (a one-dimensional Brinkman equation).

In general, second order Lagrange shape functions were used for the elements in the numerical models (this was typically the default setting). The stationary nonlinear solver was used for all stationary problems, typically with the "highly nonlinear" option selected. The nonlinear tolerance was set to 1×10^{-9} for the stationary problems. The solution form was typically set to "General" form, with all variables and expressions selected for automatic differentiation. Streamline diffusion was not used for the stationary problems. The default settings for the Jacobian solver, direct linear solver, variable scalings, assembly block size, etc. were used.

Models used for the experiments of Tallarek et al (Section 5.2.4)

For these models, Femlab 2.3 was used.

The use of an appropriate mesh was essential for the Poisson-Boltzmann and Brinkman equations, due to the very small boundary layers near the wall. In one-dimensional problems, a very dense mesh near the wall could be defined by specifying a particular mesh growth rate of $(1+g)$, and an initial (maximum) element size, w_o , near the wall, where g is some fraction specifying the increase in the element size at each step. If it is assumed that the mesh grows geometrically away from the wall, the number of elements, k , used in the mesh to reach a distance a from the wall can be calculated exactly. The problem is defined mathematically using a geometric series as

$$a = \sum_{n=0}^k w_o (1+g)^n. \quad (7.7)$$

Solving for a , one obtains

$$a = \frac{w_o ((1+g)^k - 1)}{g}. \quad (7.8)$$

The number of elements k between the wall and position a is therefore given by

$$k = \frac{\ln(\frac{ag+w_o}{w_o})}{\ln(1+g)}. \quad (7.9)$$

This makes it possible to calculate the fraction of elements in, for example, the double layer. For example, for the models used to fit the CEC results of Tallarek et al in Section 5.2.4, g was 0.01, and w_o was 1×10^{-14} . Using $a = 125\mu m$ for the column radius, there will be a total of approximately 1874 elements across the column. Assuming a Debye length of $3 nm$, using $a = 9nm$ in equation 7.9 results in $k = 915$ elements in a region approximately three Debye lengths thick. Thus, nearly 50% of the elements will be located within the double layer (which is where virtually all of the charge will be located), a region that takes up less than 0.01% of the total column radius.

In order to be able to process the numerical results in Matlab (for example, to find the

concentration profile using equations 5.15 and 5.16), the numerical data was retrieved using the following extract of Matlab code:

```
fem_r = fem.mesh.p(1:length(fem.mesh.p));

num_points = length(fem_r);
num_sol_points = length(fem.sol.u);

fem_pot = fem.sol.u(1:num_points);

fem_u = fem.sol.u(3*num_points+1:num_sol_points);

fem_pot2 = fem.sol.u(4*num_points+1:num_sol_points);

fem_r = fem_r(3:num_points)';
fem_pot = fem_pot(3:num_points);
fem_u = fem_u(1:num_points - 2);

fem_pot2 = fem_pot2(3:num_points);

fem_data = [fem_r fem_pot fem_pot2 fem_u];

fem_data = sortrows(fem_data, 1);

fem_r = fem_data(:,1);
fem_pot = fem_data(:,2);
fem_pot2=fem_data(:,3);
fem_u = fem_data(:,4);
```

The variables `fem_r`, `fem_pot`, `fem_u`, and `fem_pot2`, represent the radial position r , the potential due to ψ_w , the fluid velocity $\bar{u}$, and the potential due to ψ_o , respectively.

The convection-diffusion equation was solved numerically, using a two-dimensional axisymmetric (conservative) application mode. In order to import the one-dimensional velocity data from the Brinkman model, the following Matlab code was used, which finds the r coordinates at the inlet in the convection-diffusion application mode, and interpolates the Brinkman velocity data (using the one-dimensional mesh) onto these coordinates in the two-dimensional mesh:

```
new_r = findboundary_x(fem, -4.9999999999999996e-006);
%this is the intrinsic velocity!
new_v = postinterp(oldfem, 'u/porosity*sqrt(tort)', new_r);
```

Here, `fem` refers to the Femlab data structure for the two dimensional convection-diffusion model, and `old_fem` refers to the one-dimensional Femlab data structure. The function `findboundary_x` was used to return the coordinates of the inlet in the two-dimensional mesh:

```
function the_x = findboundary_x(fem, bnd_coord)
%returns the x coordinates for a boundary given by a y coordinate

x = fem.mesh.p(1,:);
y = fem.mesh.p(2,:);
n = find(y==bnd_coord);

the_x = x(n);
the_x = sort(the_x);
```

In order for Femlab to be able to differentiate the imported data, the following variables and differentiation rules had to be used in Femlab:

```
%interpolation settings:
```



```
fem.expr={'porosity_data_r' porosity_data_r
          'porosity_data_y' porosity_data_y
          'new_r' new_r
          'new_v' new_v
          'new_v2' 'flinterp1(new_r, new_v, r)'
          'porosity' 'flinterp1(porosity_data_r, porosity_data_y, r, 4)'}

%differentiation rules:
fem.rules = {'flinterp1(new_r,new_v,r)' '0, 0,
             flinterp1(new_r,new_v,r,1,1)'
             'flinterp1(porosity_data_r,porosity_data_y,r)' '0, 0,
             flinterp1(porosity_data_r,porosity_data_y,r,4,1)'};
```

The function `flinterp1` is a one-dimensional interpolation function in Femlab. The default setting for the interpolation order was linear interpolation, which was found to work acceptably for the interpolation of the one-dimensional velocity data. However, it was found that a higher integration order (piecewise cubic Hermite interpolation) was required to accurately interpolate and differentiate the experimental porosity data (as for example the data in Figure 5.4(a)).

The time-dependent solver routine `femtime` was used to solve the convection-diffusion problem in Femlab, using the `ode15s` solver. The absolute tolerance (maximum absolute local error) and relative tolerance (maximum allowed relative error in each time step) were 1×10^{-8} and 1×10^{-7} , respectively. The numerical results were very sensitive to the values of the absolute and relative tolerance; the tolerances were reduced to the point where further reductions had no visible impact on the final result. The use of numerical diffusion did not seem to effect the results, and thus it was not used.

In order to compare the Femlab results with the one-dimensional concentration profiles provided by Tallarek et al (such as in Figure 5.12), the two-dimensional concentration profile had to be integrated using equation 5.16. However, the numerical data first had to be extracted from the Femlab results. An interpolation grid was setup with $2.5 \mu\text{m}$ spacing in the axial direction. This is all done by the following code:

```

z = [data_x' -5e-6:2.5e-6:300e-6];

z = sort(z);

[NEW_R Z] = meshgrid(new_r, z);
[TEMP_V Z] = meshgrid(new_v, z);

p = [NEW_R(:)'; Z(:)'];

c = postinterp(fem, 'C1', p, 'solnum', t_nums(j));

c = reshape(c, size(Z));

c_new = c.*NEW_R;

    for i = 1:length(z)
        C(i) = 2*pi*my_quad(c_new(i,:), new_r); %total concentration;
    end

```

The `data_x` variable refers to the axial position of the experimental data points. The numerical integration `my_quad` was given by the following Matlab code (using a trapezoidal rule):

```

function area = my_quad(density, r);

n = length(r);
area = 0;

for i = 2:n;
    area = area + ((r(i) - r(i-1))*(density(i) + density(i-1)))/2;
end

```

Obtaining the Experimental Data

In order to be able to, for example, import the experimental porosity data, or accurately compare the numerical results with the experimental data, it was necessary to obtain an accurate estimate of the data contained in the figures from the literature. This was accomplished by taking screen captures of the figures from the literature, and importing the images into Matlab. Matlab code was written in which a user wielded a mouse pointer to select a large number (30+) of points from the desired figure. The user first had to calibrate the program by selecting three known positions in the figure and manually entering their coordinates (usually the origin and a point from each axis). The positions of all points thereafter were computed automatically. The user was able to zoom in/out using different mouse buttons, to help improve the accuracy of each point.

Figure 7.1: Comparison of the porosity data obtained using the Matlab program and the original porosity data, defined by equation 5.7. The values $A_o = 0.4$, $B = 0.5$, $C = 7$, $D = 0.1$, $E = 6$, $R = 125\mu m$, and $d_p = 41\mu m$ were used.

In order to test the accuracy of the program, porosity data was simulated using the

Bessel function model (equation 5.7). A screen capture was then taken of the resulting Matlab plot, and the program was used to obtain a number of points from the image. The resulting data was then plotted, alongside the original function. The result is shown in Figure 7.1. It can be seen that the data obtained by the program deviates imperceptibly from the actual data.

Modelling the Nitrocellulose Microfluidic Devices (Section 5.3)

The nitrocellulose devices from Section 5.3 were modelled using Femlab 3. The Electrostatics application mode was used to find the electric field between the electrodes, the Navier-Stokes application mode was used to find the fluid flow, and the Convection-Diffusion application mode was used for the dye movement. To save memory, the Electrostatics application mode was only solved in the region between the electrodes, while the Convection-Diffusion application mode was only solved in the bottom channel (where the dye was located).

Scalar expressions that called a Matlab function were used to determine the effective permeability and effective charge densities (when applicable), due to the heterogeneous nature of the membranes, for the different regions. Subdomain expressions were used to assign the permeability, effective charge density, porosity, etc. to their proper values in each region, so that the model could use the same variables names in the equations for each subdomain.

The dimensions of the experimental devices themselves were originally measured using a caliper. However, due to inconsistencies in repeated measurements, the device dimensions were instead measured using pixel distances in the images themselves, using the set electrode spacing of 4.5 mm as a reference. The caliper measurement of the right hand portion of the load, which was outside of the camera viewpoint, was the only caliper measurement that was used. The experimental images were imported into Femlab using a Matlab script (as a Subdomain expression), using the following code:

```
function D_out = image_test_Device1(t_num, x, y)
```

```

if t_num == 31.85
    im_name = 'NF_31s_85ms_009_cut.bmp'
    data = [1.0000000000000000 -8.7e-3  0
            2.0000000000000000  7.3e-3  0
            3.0000000000000000  7.3e-3 -5.7e-3
            4.0000000000000000 -8.7e-3 -5.7e-3];

    data_x = data(:,2);
    data_y = data(:,3);
    X1 = (data_x(1)+data_x(4))/2;
    Y1 = (data_y(1)+data_y(2))/2;
    X2 = (data_x(2)+data_x(3))/2;
    Y2 = (data_y(3)+data_y(4))/2;
elseif...

    etc...

end

dye_red = imread(im_name);

dye_gray_comp = rgb2gray(dye_red);

D_vals = 1-im2double(dye_gray_comp);

[y_size x_size] = size(D_vals);

y_vals = Y1:(Y2-Y1)/(y_size-1):Y2;

x_vals =X1:(X2-X1)/(x_size-1):X2;

[X_VALS Y_VALS] = meshgrid(x_vals, y_vals);

```

```
D_out = interp2(X_VALS, Y_VALS, D_vals, x, y);
D_out(find(isnan(D_out))) = 0;
```

This function imported the desired experimental result (which was cropped so as to contain only the bottom channel), converted it to grayscale, and then inverted the shading (so that the lightest areas were attributed to the region with the highest concentration). This image was then interpolated onto the finite element mesh using the `interp2` function.

The stationary nonlinear solver (set to highly nonlinear) was used for the electrostatics and the fluid flow problems, with a relative tolerance of 1×10^{-6} , and the default settings for the linear system solver. The time-dependent solver was used for the convection-diffusion problem, with an absolute tolerance of 1×10^{-6} and a relative tolerance of 1×10^{-5} , and with artificial stabilization turned off. The solver was set to find the solution at the same times at which the experimental images had been taken (although the solver algorithm would use many more points than just these few). The initial value was set to “Current solution”, and the fixed solution/linearization point setting was kept at its default value of “initial value”.

For the case where the applied voltage decayed with time, the time-dependent solver was used for all three application modes, using the same settings as described in the previous paragraph. The initial value for the Electrostatics application mode was set to “Initial value expression”, but the other application modes used “Current solution” for the initial value and “Current solution- Solution at time: All” for the fixed solution/linearization point setting.

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