



**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**CAPILLARY FILLING, EVAPORATION
AND CONDENSATION IN NANOCHANNELS**

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SCHOOL OF MECHANICAL
AND AEROSPACE ENGINEERING
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Capillary Filling, Evaporation and Condensation in Nanochannels

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Abstract

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Investigation of the transport effects in nanochannels is an interesting topic, especially in recent years, when new micro/nano technologies allow the fabrication of nanoscale structures that can replace the traditional nanoporous materials such as paper, silica gel, alumina, or cellulose. Key transport effects such as capillary filling, gas absorption in liquid, evaporation and condensation in nanochannels are significantly different from those in larger channels, e.g. microchannels. This thesis presents the theoretical and experimental investigations of these effects.

To prepare for the subsequent experiments, nanochannels were fabricated in silicon and polymer. Silicon nanochannels were fabricated with a silicon wafer and a Pyrex glass wafer. The silicon wafer was cleaned to remove the contaminants. The nanopatterns were created on the wafer surface by photolithography and reactive ion etching (RIE). Deep reactive ion etching (DRIE) was used to create the access holes from the back side. The photoresist was removed, then a Pyrex glass wafer was sealed on top of the channels by anodic bonding. Polymeric planar nanochannels were fabricated using hot embossing and thermal bonding on polymer films and plates. The mold for hot embossing was fabricated on a silicon wafer using photolithography and RIE, followed by surface treatment and Teflon coating. Poly(methyl methacrylate) (PMMA) films with a thickness of 250 μm and PMMA plates with a thickness of 1 mm were used to make the channels. Access reservoirs were created using a laser cutter. Patterns on the silicon mold were transferred to the polymer surface by

a hot embossing process. Next, another piece of PMMA was bonded to the first piece by thermal bonding to make closed channels. The result shows that open planar channels with the depth down to 30 nm can be fabricated on PMMA substrate. The width and the depth of the channels agree well with the dimensions on the mold. Closed planar nanochannels with the depth of 300 nm were fabricated successfully with polymer film and nanochannels with the depth of 220 nm were fabricated with polymer plate. Temperature and pressure were controlled and recorded continuously during both the hot embossing and thermal bonding processes.

A model was built to describe the capillary filling process in a nanochannel with consideration of electrokinetic interactions. In larger scale channels, where the thickness of electrical double layer (EDL) is much smaller than the characteristic length, which is typically the smallest dimension of the channels, the formation of the EDL plays a negligible role in fluid flow. However, in nanochannels, where the EDL thickness is comparable to the characteristic length, the formation of the EDL influences the filling flow of the fluid. This theoretical result predicts that the filling process follows the Washburn equation, where the filling length of the fluid is proportional to the square root of time, but with a lower filling speed. The reduction in filling speed of the fluid due to the electrokinetic interactions is called electroviscous effect because it can be visualized by an increase in the apparent viscosity. The theory also shows that the electroviscous effect is most significant if the ratio between the channel height (h) and the Debye length (κ^{-1}) reaches an optimum value (i.e., $\kappa h \approx 3.8$). The apparent viscosity is higher with higher zeta potential and lower ion mobility. The filling experiments with electrolytic and nonelectrolytic solutions in polymeric nanochannels were carried out. The filling processes were observed and recorded. Filling distances were measured, and filling speeds were derived. The filling speed was found to be significantly lower than predicted by the mathematical model based on electroviscous effect. The discrepancy suggests that, beside the electroviscous effect, there are other phenomena which contribute to the reduction of capillary filling speed in nanochannel. Formation of air bubbles, evaporation and condensation in nanochannels during the filling process were observed during the filling process.

To investigate the interactions between liquid, gas and solid phases in nanochannels, the experiment of capillary filling in closed-end silicon nanochannels with different lengths

was carried out. The experimental results show that the filling process consists of two stages. In the first stage, the capillary filling process resembles that in an open-end nanochannel. In the second stage, the meniscus does not stop at the value predicted by the model for large-scale channels, but continues to fill until the end of the nanochannel. The remaining gas trapped in the nanochannels slowly dissolves in the liquid. In this stage, the experimental data fit well to a mathematical model which considers the gas absorption and diffusion, described by Henry's law and Fick's law respectively.

Experimental results of drying of ethanol in nanochannels were obtained. The drying speed was found to be independent to the total channel length. This result qualitatively agrees with the theoretical model based on diffusion. In addition, the condensation of liquid in nanochannels was observed when a stream of evaporated vapour was blown across the entrance of the nanochannels. The advancing movement of the meniscus could be described using the difference in curvature of the menisci at the two ends of the liquid column, together with the Langmuir's law and Kelvin's law of condensation.

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List of Symbols

Greeks

Λ_m	Molar conductivity of a monovalent electrolyte
Φ_m	Mass flux of gas molecules, see equation (5.16)
α	Dimensionless parameter, see equation (5.10)
β	Dimensionless parameter, see equation (5.22)
γ	Heat capacity ratio
δ_b	Longitudinal electric charge density of the fluid body
δ_w	Longitudinal electric charge density of the channel wall
ϵ	Relative permittivity of the fluid
ϵ_0	Permittivity of vacuum, $8.85 \times 10^{-12} \text{ CV}^{-1}\text{m}^{-1}$
ϵ_p	Pressure dependent error level, page 121
ϵ_{psat}	Saturation pressure dependent error level, page 122
ϵ_T	Temperature dependent error level, page 122
ζ	zeta potential
η	Dimensionless parameter, see equation (4.64)
η_1	Dimensionless parameter, see equation (4.64)
η_2	Dimensionless parameter, see equation (4.64)

θ	Contact angle
θ_a	Apparent contact angle
κ	Inverse of the Debye length
λ	Total conductivity of the electrolyte
λ_i	Individual contribution of ionic species i to the conductivity
λ_m	Mean free path of the molecules
μ	Dynamic viscosity
μ_a	Apparent dynamic viscosity
v_i	Electric mobility of ionic species i
ξ	Auxiliary variable, see equation (4.44)
ρ_q	Charge density
ρ_m	Mass density of the fluid
σ	Surface tension
σ_a	Apparent surface tension
τ	Dimensionless filling time, see equation (5.24)
$\tau_{\text{capillary}}$	Characteristic time of capillary filling, see equation (5.10)
$\tau_{\text{diffusion}}$	Characteristic time of diffusion, see equation (5.22)
υ	Friction coefficient of the fluid, see equation (6.3)
χ	Auxiliary variable, see equation (4.37)
ψ	Electrostatic potential across the channel height
Romans	
$\mathcal{A}$	Area

A, B, C, D, E Auxiliary variables, see equation (4.37)

D_d Diffusion coefficient

D_F Fickian diffusion coefficient

D_K Knudsen diffusion coefficient

$\mathbf{E}$ Electric field strength vector, see equation (2.4)

E_s Streaming electric field strength

F_v Viscosity force act on the fluid

F_e Electric force

F_s Surface force

G Electroosmotic coefficient, see equation (2.10)

I Electric current, see equation (2.16)

I_c Conduction current

I_0, I_1 Bessel functions, see equation (2.11)

I_s Streaming current

I_{total} Total current entering the control volume

L Channel length

L_e Equivalent entrance length, see equation (4.68)

N Number of particles, see equation (6.1)

N_A Avogadro number

ΔP Pressure difference

R Radius of a channel

T Room temperature

T_g	Glass transition temperature
U	Fluid flow, see equation (2.16)
U_s	Streaming potential
V_M	Molar volume of liquid
a	Washburn coefficient, see equation (4.69)
c_0	Concentration at the channel entrance, see equation (5.15)
d	Diameter of molecules
e	Elementary charge, 1.602×10^{-19} C
f	Arbitrary vector function
h	Channel height
k	Boltzmann constant, 1.31×10^{-23} Jmol ⁻¹ K ⁻¹
k_H	Henry coefficient, see equation (5.15)
m	Mass
m_0	Initial mass
m^*	Dimensionless mass, see equation (5.22)
n_i^0	Concentration of ionic species i
n_+^0	Bulk concentration of cations
n_-^0	Bulk concentration of anions
p	Pressure
p_0	Initial pressure
p'_{sat}	Saturation pressure above a curved surface, see equation (6.25)
q_a	Accumulated charge

q_{total}	Total charge in the control volume
r	Radial coordinate in a channel
r_1, r_2	Radii of curvature, see equation (4.1)
$\mathbf{t}$	Time data vector, see equation (4.68)
t	Time value
$\mathbf{t}'$	Entrance length effect corrected time data vector, see equation (4.68)
t_0	Initial time constant, see equation (4.57)
t^*	Dimensionless time, see equation (5.9)
u	Fluid velocity
$\bar{u}$	Average velocity across the channel, meniscus velocity, see equation (4.3)
v^*	Dimensionless velocity, see equation (5.26)
w	Channel width
$\mathbf{x}$	Filling length data vector, see equation (4.68)
x	Coordinate along the channel length
$\mathbf{x}'$	Entrance length effect corrected filling length data vector, see equation (4.68)
x^*	Dimensionless length, see equation (5.8)
y	Coordinate across the channel height
z_i	Charge number of ionic species i
z_+	Charge number of cations
z_-	Charge number of anions
Accents	
$-$	Average value across the channel height

·	Time derivative
^	Divide by the channel width
~	Normalized value of electric potential by multiplying by e/kT

Acronyms

AFM	Atomic Force Microscope
CR	Compression ratio
DIW	Deionized water
DRIE	Deep reactive ion etching
EDL	Electric double layer
IC	Initial condition
IPA	Isopropanol
MD	Molecular dynamics
ODE	Ordinary differential equation
PB	Poisson-Boltzmann
PC	Polycarbonate
PMMA	Poly(methyl methacrylate)
RIE	Reactive Ion Etching
UV	Ultraviolet

Chapter 1

Introduction

1.1 Background

The latest advances in fabrication technologies and metrology in nanoscale open a new horizon in exploring the fine structure of the materials. With new ultraprecision technologies and micromachining processes such as photolithography or reactive ion etching (RIE), channels with at least one dimension below 100 nm can be fabricated. These channels are termed in this work as nanochannels. These new nanoscale devices find plenty of applications in biomedical analysis, fuel cell, and other fields.

For example, recent research works revealed that chromatography in nanochannels can lead to much more sophisticated applications than what traditional chromatography can offer [1]. Traditional chromatography drives the sample in a mobile phase through a porous material served as the stationary phase, or matrix. Difference in affinity of the components of the sample makes them migrate to different distances. The pattern left by the migration of the mobile phase in the matrix therefore reveals the information about the composition of the sample. The technique is limited by the random structure of the matrix. Most results are derived by the pattern comparison technique. A deterministic structure provides two important improvements. Firstly, the deterministic fabricated structure of the matrix can be made to be highly anisotropic. The directional difference in properties of the matrix improves the options for separation of compositions. Beside the distance-based separation, direction-based separation is now allowed. Secondly, the size and shape of the structure can

be fabricated and measured to a very high precision. Therefore, the quantitative theory in fluid dynamics in nanoscale can be applied to improve the reliability of the chromatography technique. Because the size of the macromolecules such as proteins or DNAs is usually in nanoscale, the structures at nanoscale are particularly suitable to “sieve” these molecules. For instance, Bakajin et. al. [2] demonstrated the separation of 100 kbp DNA in 10 seconds using electrophoretic movement induced by a switching electric field in a nanoscale pillar array. Han et. al. [3] introduced a technique to separate DNAs by entropic trap, which is a region of alternated shallow and deep regions in nanoscale. Using micromachining technology, it is also possible to integrate electronic components in nanochannels. Then, the unique electric polarization property of fluid in nanoscale can be employed to control the flow of ions and particles [4–6]. This ability suggests new techniques in flow control, purification, and concentration enhancement. The applications of fluid dynamics in nanochannels are still continuously developing [7].

Beside the technological challenge of miniaturization of the matrix structure, one of the key difficulties in implementing the ability of the nanochannels in practical application is the lack of theoretical basis of fluid dynamics in nanoscale.

Although the first principles on the theory of fluid mechanics at nanoscale (typically 1-100 nm) have been developed from around the beginning of 19th century [8], those principles are difficult to verify experimentally. Compared to the counterparts in microchannels or in larger channels, the fluids in nanochannels exhibit a lot of new properties. Some of them were quantitatively investigated, such as the electroviscous effect, the others were only described mainly by qualitative observation and hypotheses, such as the formation of bubbles occurs during the capillary filling. Even quantitative analyses also rarely show good agreement to experimental data. Empirical fitting factors are usually introduced to the theory to fit the theoretical prediction to the experimental results [9]. In such a situation, efforts toward development and verification of fluid dynamic theories in nanoscale are both interesting and practically promising. The research field of nanofluidics investigates the characteristics of fluids that are confined in nanoscale structures and their manipulation.

Transport phenomena in nanoscale structure are generally more complicated than those in large scale. Beside the physics governing the transport phenomena in the large scale such as surface tension, evaporation, and condensation, other phenomena such as selective

ion absorption, van der Waals attraction etc. are also significant. Although the theories that consider such phenomena are quite well established, the experimental confirmations are actually limited. The objective of the present thesis is the investigation of several significant transport phenomena, such as capillary filling and electroviscous effect as well as relevant phenomena such as gas absorption into liquid, evaporation, and condensation.

At the solid/liquid interface, due to the difference in electric potential between the solid and the liquid, the ions redistribute and form an electric double layer (EDL). The thickness of the EDL is usually represented by the Debye length. The formation of EDL and the Debye length are described by Poisson-Boltzmann (PB) equation. The dimension of a nanochannel is comparable to the Debye length. As a result, the effect of the EDL, which is negligible for larger scale fluid mechanics, becomes significant in nanoscale. Fluids display some unique characteristics which cannot be observed at larger scale. For instance, the ions redistribute themselves throughout the fluid body. The fluid responds to external electromagnetic field, and itself also creates an electromagnetic field. The distribution of ions is described by the PB equation, and the force interaction is governed by the Coulomb's law. Although the equations describing the above phenomena are well-known, the exact solutions can only be found for limited cases. Generally, either approximate solution or numerical solution is available. For each specific case, a simplified model or numerical scheme may be more appropriate. Consequently, fluid flow in nanoscale requires a deeper and more rigorous treatment.

Recently, formation and disappearance of air bubbles are investigated systematically in capillary filling experiment in nanochannels. Some authors attribute this phenomenon to the discrepancy between theoretical and experimental results. The formation and disappearance of air bubbles closely relate to the absorption of gas into liquid. In macro scale, the absorption is negligible. However, in nanoscale, due to the high Laplace pressure, i.e., higher than the saturation pressure, gas absorption must be considered. Therefore, it is necessary to design an experiment to quantitatively measure gas absorption in nanochannels.

The mean free path of the typical molecules is at nanoscale leading to a different diffusion process in nanochannels. In addition, a small radius of curvature of the meniscus causes a modification in the saturation vapour pressure. Hence, the condensation rate of the vapour is expected to be different than in larger scale. Within this project, experiments were

designed to provide data for the investigation of the evaporation of liquid and the condensation of vapour. Mathematical models were built to describe these phenomena. Although more efforts should be carried out in future for a full understanding of these phenomena, the results in this thesis set the foundation for further research in nanofluidics.

1.2 Objectives and Scopes

As mentioned above, the objective of this project is the investigation of several transport phenomena in nanochannels such as capillary filling, gas absorption, evaporation, and condensation.

The first scope of this project is to establish the fabrication of nanochannels in silicon and polymers. The nanochannels were subsequently used for a variety of experiments on transport phenomena in nanoscale.

The second scope is to revisit the theory on several significant transport phenomena in nanochannels such as capillary filling, absorption, and condensation, and evaporation of liquid.

Chapter two reviews the state-of-the-art of transport phenomena in nanochannels in both analytical and experimental fronts. Simulation results and advances in fabrication technologies of nanodevices are also reviewed. Lastly, a review on recent applications of nanofluidics is also provided.

Chapter three discusses the fabrication of polymeric and silicon nanochannels. The materials and fabrication procedures are introduced. Important parameters of the in fabrication process are also discussed.

Chapter four examines the capillary filling process in open-end nanochannels. A theoretical model was built to describe the contribution of electroviscous effect on capillary filling in nanochannel. Numerical and asymptotic solutions were obtained. The electroviscous effect was then compared to experimental data to evaluate its significance. Experiments were carried out with polymeric nanochannels to provide data for validation of the theories.

In chapter five, capillary filling in closed-end nanochannels was investigated. This investigation highlights the importance of gas absorption into liquid. This phenomenon was

neglected in all previously reported models of liquid transport in nanochannels. Quantitative measurements of filling lengths versus time were obtained for ethanol and isopropanol. The behaviour of the meniscus during the filling process and the formation of air bubbles were recorded and qualitatively investigated. A simple model was developed based on the absorption and diffusion of gas in liquid to predict the position of the meniscus.

Chapter six discusses the drying process in nanochannels. A brief review on different diffusion regimes is provided in this chapter. A model on drying in nanochannels is established based on diffusion theory. This theory was then compared to experimental data. This chapter also introduces an investigation on the condensation process in nanochannels. Condensation was observed at the entrance of the nanochannel with vapour flow passed through the entrance. The condensation was explained by a model considering the radius of curvature of the meniscus, Kelvin's law on the variation of saturation pressure and Langmuir's law on the condensation rate. The theoretical results are then compared to experimental data.

The last chapter summarizes up the results and conclusions from all previous chapters. This chapter also evaluates all contributions of this thesis as a whole. From this point of view, beside the new contributions, the author also points out the areas that need further investigations in future projects, which is necessary for a complete understanding of mass transport in nanochannels.

Chapter 2

Literature Review

2.1 Transport Phenomena in Nanochannels

2.1.1 Electric Potential Distribution

As the characteristic length reduces to the scale of several nanometers, mass transport is governed by unique characteristics. Due to the small scale involved, the Reynold number is usually less than unity and laminar flow governs. The area-to-volume ratio increases. Consequently, effects related to surface such as surface tension, absorption etc. become significant. Furthermore, if the characteristic length is comparable to the Debye length, electrokinetic effects are apparent and lead to phenomena such as electrophoresis and electroosmosis, which have been widely applied in many microfluidic devices. The electrokinetic properties of a fluid are caused by the formation of the electric double layer (EDL). At the interface of a fluid and a solid, non-electrical affinities such as chemical affinity, absorption, and defects in crystal structure cause ions to attach to the solid surface [10]. This process is highly selective, so only certain types of ions can attach to the surface better than the others. This process makes the surface gain an electric potential which is different than the bulk fluid potential. The potential at the shear plane is called zeta potential. Difference in electric potential between the solid surface and the bulk fluid creates an electric field, and hence, causes ions in the fluid to redistribute. The redistribution of ions in the fluid is governed by Coulomb's law and Poisson-Boltzmann (PB) equation. Because the electric charge density at any point in the fluid is generally not zero, the fluid now can respond to

an external electric field.

The movement of fluid under an applied external electric field is called electroosmosis, while the movement of small particles submerged in the fluid under an applied external electric field is called electrophoresis. The zeta potential depends on the solid material and fluid composition. There are evidences showing that the zeta potential can be controlled by traverse external electric field [11]. The zeta potential also depends on other environmental conditions such as the formation of bubbles [12]. According to Anfken and Weber [13], the static electric charge of the surface attracts ions with opposite signs. An ion layer accumulating near the surface creates the EDL. The EDL can be described by the distribution of electric charge density, especially at the zone near to the surface. Such density profile is governed by Coulomb's law and PB equation on distribution of energy level. For a binary electrolyte ($z_+ : z_-$), the PB equation reads:

$$\begin{cases} \nabla^2 \tilde{\psi} &= -\frac{\rho_q e}{\epsilon \epsilon_0 k T} = -\frac{e^2}{\epsilon \epsilon_0 k T} [n_+^0 z_+ \exp(-z_+ \tilde{\psi}) + n_-^0 z_- \exp(-z_- \tilde{\psi})] & (2.1a) \\ \rho_q &= -\epsilon \epsilon_0 \nabla^2 \psi & (2.1b) \end{cases}$$

where ψ is the electrostatic potential, ρ_q is the charge density, $e = 1.602 \times 10^{-19}$ C is the elementary charge, ϵ is the relative permittivity of the fluid, $\epsilon_0 = 8.854 \times 10^{-12}$ CV⁻¹m⁻¹ is the permittivity of vacuum, z_+ and z_- are the charge numbers, n_+^0 and n_-^0 are the bulk cation and anion concentrations respectively, $k = 1.305 \times 10^{-23}$ Jmol⁻¹K⁻¹ is the Boltzmann constant, T is the environment temperature, and $\tilde{\psi} = \psi e / k T$ is the normalized electrostatic potential. Based on the equation system (2.1), the Debye length $\kappa^{-1} = \sqrt{(\epsilon \epsilon_0 k T) / (n_+^0 z_+^2 + n_-^0 z_-^2)}$ is usually used to represent the thickness of the EDL, although there were arguments that the Debye length does not represent well the thickness of the EDL [14]. This set of equations is non-linear, so it does not have a general analytical solution. However, for a single flat wall submerged in an infinite fluid solution, the analytical solution can be found for both symmetric ($z_+ = -z_-$) and asymmetric ($z_+ \neq -z_-$) binary electrolytes [15–17]. The boundary condition in this case is $\psi = \zeta$ at the shear plane (near to the wall surface) and towards zero at infinity. For a more complicated geometry, it is much more difficult to get an analytical solution, especially for asymmetric electrolytes. In such cases, alternative solutions can be considered. Firstly, numerical solutions can be

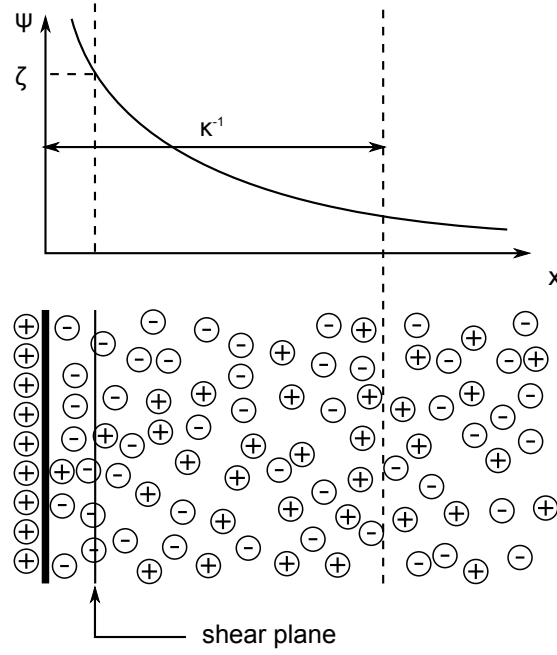


Figure 2.1: Ion distribution and electric potential distribution in the case of single flat wall with positive zeta potential.

achieved. By discretisation of the solution domain, the differential equations can be transformed into a system of algebraic equations and then solved numerically. This method can give useful results, and the accuracy can be determined in advance, but high computing capacity is required for a complicated geometry. Figure 2.1 illustrates the concepts of zeta potential and Debye length using electric potential distribution in the case of a single flat wall.

Another approach is to get the approximation for an analytical solution. For low electric potential (typically $\psi \leq \zeta \leq 26$ mV) it is suitable to apply the linear approximation $\sinh \tilde{\psi} \approx \tilde{\psi}$, so that the equation system can be linearised and therefore analytically solvable for any geometry. However, the low potential approximation has limited practical use because many solid/electrolyte pairs have a high zeta potential. For a parallel slit-shaped channel, the symmetry condition $\nabla \psi|_{\text{center}} = 0$ can be applied. The analytical solution for this case was expressed in term of elliptic functions [18, 19].

Using the low-potential approximation, the solution of PB equation for a slit-shaped channel with boundary condition $\tilde{\psi} = \tilde{\zeta} = \zeta e/kT$ at the wall surface and $\nabla \tilde{\psi} = 0$ at the

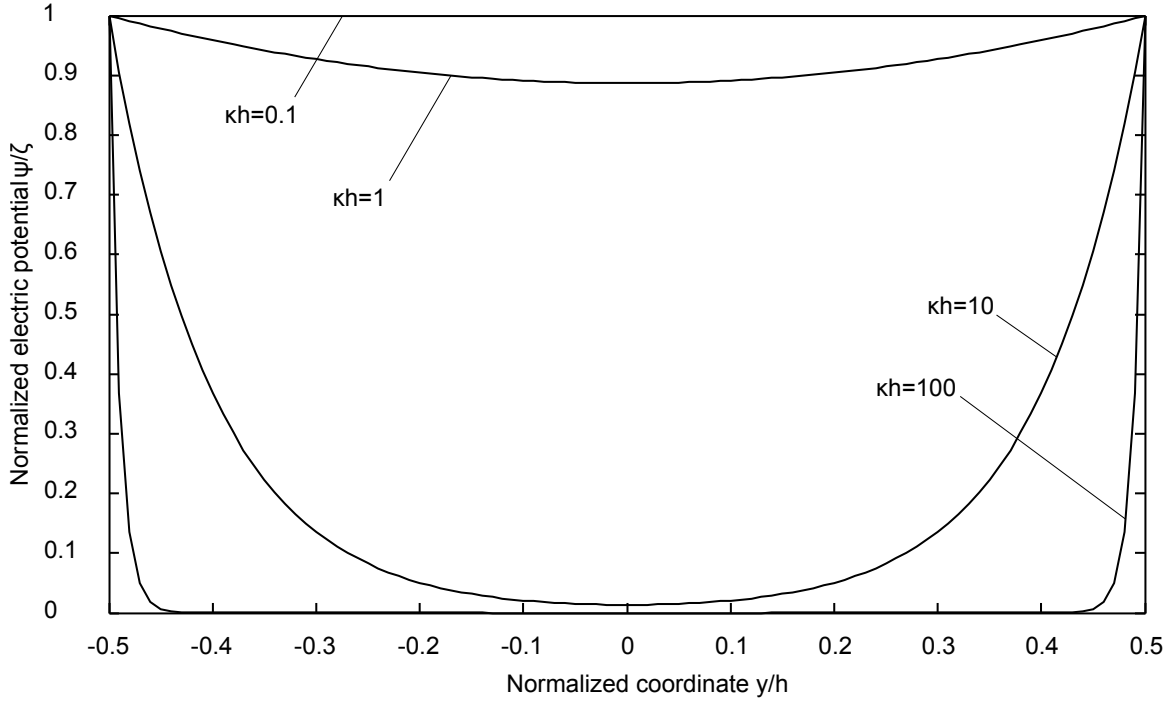


Figure 2.2: Electric potential distribution in a slit-shaped channel with low potential approximation. The results are plotted for cases ranging from a thin EDL ($\kappa h \gg 1$) to an overlapping EDL ($\kappa h \ll 1$).

centerline, with the normalized zeta potential $\tilde{\zeta}$ [16], is:

$$\tilde{\psi}(y) = \tilde{\zeta} \frac{\cosh[-\kappa y]}{\cosh \frac{\kappa h}{2}}. \quad (2.2)$$

The electric potential distribution (2.2) is illustrated in Fig. 2.2 for cases ranging from a thin EDL ($\kappa h \gg 1$) to an overlapping EDL ($\kappa h \ll 1$). Rice and Whitehead [20] provided the solution for the case of a cylindrical nanochannel in term of zero order modified Bessel function

$$\tilde{\psi}(r) = \tilde{\zeta} \frac{I_0(\kappa r)}{I_0(\kappa R)} \quad (2.3)$$

where R is the radius of the nanochannel. The electric potential distribution (2.3) is illustrated in Fig. 2.3.

Li and Yang [21] reported the solution for rectangular microchannels. Low potential approximation is valid for very narrow channels as long as the condition $z\tilde{\psi} < 1$ is satisfied. At room temperature $T = 298$ K, the low-potential approximation requires that zeta potential is less than 26 mV [16]

Petsev and Lopez [22] suggested an alternative solution for the case of an EDL thick-

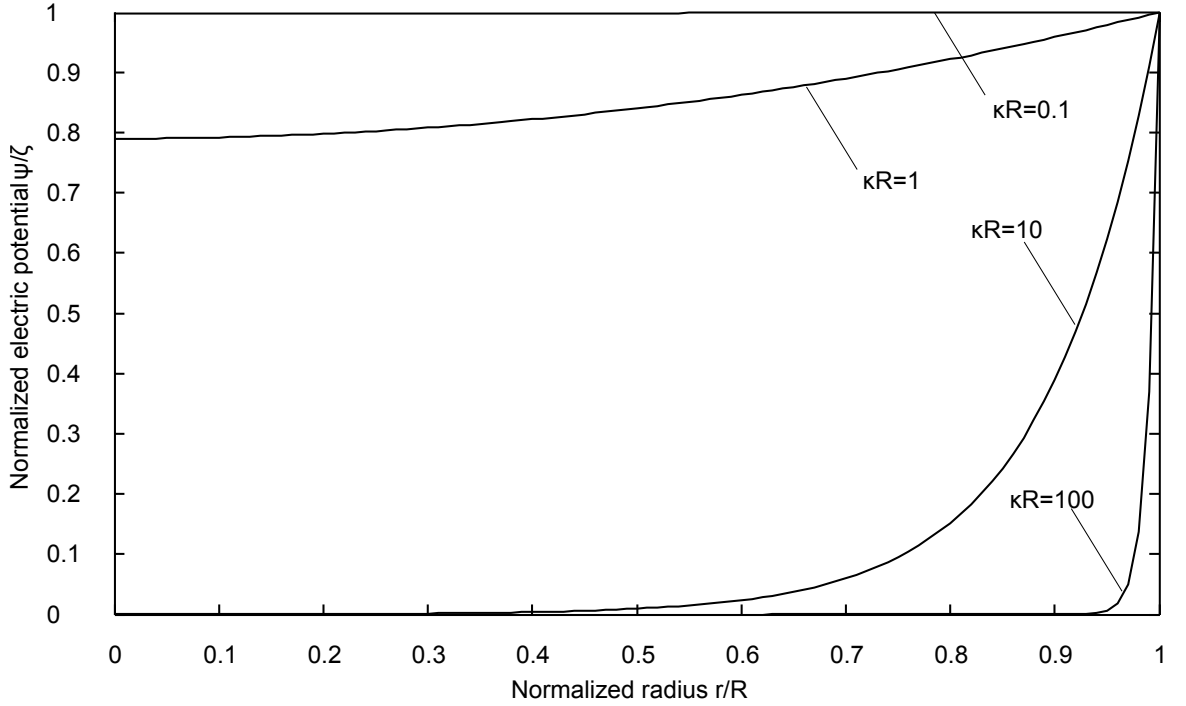


Figure 2.3: Electric potential distribution in a cylindrical channel with low potential approximation. The results are plotted for cases ranging from thin EDL ($\kappa R \gg 1$) to overlapping EDL ($\kappa R \ll 1$).

ness much smaller than the channel width. In this case, the interaction between the two EDLs is considered as negligible. The final potential distribution is taken as superposition of two single wall EDL potential distributions, which can be found analytically. Thin EDL approximation was used by Levine [23] to construct the potential distribution in a cylindrical nanochannel. In that model, the inner part of the nanochannel is divided into two regions. The first region is near to the wall (inner region), where the thin EDL approximation can be used. The second region is far away from the wall (outer region). Thin EDL approximation is not applicable here, but the potential drops enough to justify the low-potential approximation. The solutions for these two regions are then combined by matching asymptote method to get the final distribution [22, 24, 25].

2.1.2 Electroosmotic Flow

The flow of electrolytic fluids in a nanochannel is described by the Navier-Stokes (NS) equation [26, 27]:

$$\mu \nabla^2 v = \nabla p + \rho_e \mathbf{E} = \nabla p - \epsilon \epsilon_0 \nabla^2 \psi. \quad (2.4)$$

This equation shows that the fluid can be driven by a pressure gradient or by applying an electric field $\mathbf{E}$. As the size of the channel decreases, there are difficulties to implement pressure-driven concept to manipulate the fluid flow. Therefore, electroosmosis is a popular method to drive a fluid in microchannels and nanochannels. Fluids can be driven simply by applying a voltage across the channel [28]. In the absence of an applied pressure, the NS equation becomes :

$$\mu \nabla^2 v = \rho_e \mathbf{E} = -\epsilon \epsilon_0 \nabla^2 \psi . \quad (2.5)$$

The solution of this equation is the velocity profile of the fluid, from which other quantities such as average velocity or flow rate can be determined.

Smoluchowski [29] reported the solution for electroosmotic flow in a straight channel with a uniform electric field applied along the channel. The analysis showed that the velocity profile has the same form as the electric potential profile. This result is valid for a constant dynamic viscosity μ and a constant electric permittivity ϵ [26, 27]. The velocity profile is then given by:

$$u(r) = -\frac{\epsilon \epsilon_0 \zeta}{\mu} |\mathbf{E}| \left[1 - \frac{\psi(r)}{\zeta} \right] . \quad (2.6)$$

From that velocity distribution, the average velocity can be obtained as:

$$\bar{u} = \frac{1}{\mathcal{A}} \int_{\mathcal{A}} u d\mathcal{A} = -\frac{\epsilon \epsilon_0 \zeta}{\mu} |\mathbf{E}| (1 - G) \quad (2.7)$$

with

$$G = \frac{1}{\zeta h} \int_{-h/2}^{h/2} \psi dy . \quad (2.8)$$

Determining the average velocity $\bar{u}$ now is equivalent to determining the coefficient G . The formula of G depends on the formula of the electric potential ψ . If the EDL is much thinner than the smallest dimension of the channel, G becomes negligible [26, 27, 29]. Burgreen, Nakache [30] and Hildreth [31] gave the formula of G for the symmetric solution in slit-shaped nanochannels in the form of the following integral:

$$G(\zeta, \kappa h) = \frac{2}{\kappa h \zeta} \int_{\tilde{\psi}_m}^{\tilde{\zeta}} \frac{(z \tilde{\psi}) d(z \tilde{\psi})}{\sqrt{2[\cosh(z \tilde{\psi}) - \cosh(z \tilde{\psi}_m)]}} \quad (2.9)$$

whose value can be determined numerically. Levine et al. [23] also presented an alternative formula in term of series. The formula (2.9) is based on the exact solution of the electric potential profile. With state-of-the-art high-performance computing, a numerical result

might not be too difficult to achieve. However, these two forms are quite challenging to use in further analysis, so various approximations were often used. Substituting the low-potential approximation (2.2) into (2.8) for a slit-shaped nanochannel, the formula for the coefficient G is:

$$G = \frac{1}{h} \int_{-\frac{h}{2}}^{\frac{h}{2}} \frac{\cosh(-\kappa y)}{\cosh \frac{\kappa h}{2}} dy = \frac{2}{\kappa h} \tanh \left(\frac{\kappa h}{2} \right). \quad (2.10)$$

This formula is simple and suitable for further analysis. However, (2.10) is only applicable for channels with zeta potential lower than 26 mV, which is not always practical. Petsev [32] gave an approximation for slit-shaped nanochannel with a thin EDL. This approximation is valid for an arbitrary high potential, as long as the condition $\kappa h > 4$ is satisfied. The formula of the coefficient G is given in term of Lerch's transcendent, which can be easily evaluated numerically. One interesting point is that this formula agrees well with Eq. (2.10) for the case of low zeta potential, even for $\kappa h < 4$. Therefore, Petsev formula has a wider use than Eq. (2.10), although it is more complicated for further analysis.

Applying low-potential approximation to a cylindrical nanochannel, the coefficient G can be expressed by the first and zero order Bessel function I_1, I_0 [23]:

$$G = \frac{2I_1(\kappa R)}{\kappa R I_0(\kappa R)} \quad (2.11)$$

where R is the radius of the channel. This approach has the same limitation as that of the slit-shaped channel, so that it is only applicable for liquid-solid interfaces that have a zeta potential less than 26 mV, which are not commonly found. Figure 2.4 illustrates the coefficient G versus the normalized EDL thickness for slit-shaped channels and cylindrical channels. On the one hand, the coefficient G becomes negligible for both cases when the normalized EDL thickness reduces. On the other hand, when the normalized EDL thickness increases, the coefficient G approaches 1, which suppresses the electroosmotic flow. Petsev and Lopez [22] suggested a solution using thin-EDL approximation for a cylindrical nanochannel. The method is similar to the case of a slit-shaped channel, where the space in the nanochannel is divided into inner and outer regions. The solution is assumed to depend only on the radial position and the ratio κR between the radius of the nanochannel and the Debye length. Under this assumption, the first order approximation is determined by the zero order Bessel function. After matching the two solutions in two regions, the final

solution is

$$\tilde{\Psi} = \tilde{\Psi}^{(0)} + \frac{1}{\kappa R} \tilde{\Psi}^{(1)} . \quad (2.12)$$

Applying

$$G = \frac{1}{\zeta \mathcal{A}} \int_{\mathcal{A}} \tilde{\Psi}(r) d\mathcal{A} . \quad (2.13)$$

to the case of the cylindrical nanochannel leads to:

$$G = \frac{2}{\zeta R^2} \int_0^R \tilde{\Psi}(r) dr = \frac{2}{\zeta R^2} \int_0^R \left[\tilde{\Psi}^{(0)}(r) + \frac{1}{\kappa R} \tilde{\Psi}^{(1)}(r) \right] r dr . \quad (2.14)$$

This formula can be computed analytically although the final expression is complex. Thin-EDL approximation for micro/nanochannels provides a faster way to obtain the numerical value of G compared to the numerical solution of the PB equation [22]. Figure 2.5 depicts coefficient G as a function of normalized EDL thickness using the thin-EDL approximation and with the normalized zeta potential of $\tilde{\zeta} = 1$. Figure 2.5 shows that this approximation is not applicable for the case of a thick EDL ($\kappa R < 1$) because G should be less than or equal to unity. However, for a thin EDL, this approximation approaches the low-potential approximation.

2.1.3 Capillary Filling

Capillary filling plays an important role in analytical chemistry. For instance, the planar chromatography based on capillary filling phenomenon to drive mobile phase through a porous material, such as paper, silica gel, alumina, or cellulose, which serve as the stationary phase. Difference in affinities is then used to separate the analytes. The advances in micro/nanotechnologies promise the replacement of traditional stationary phase in planar chromatography by more deterministic, controllable nanostructures, such as nanochannel. However, many aspects of capillary filling in nanochannels are still under investigation. Understanding capillary filling in nanochannel contributes to the further development of analytical technology.

Washburn [33] provided a simple formula to describe the capillary filling process in porous materials. The formula states that the filling distance is proportional to the square root of time. To verify this formula in nano scale, many theoretical and experimental works on capillary filling in nanochannel have been performed. Tas et al. [34] found that water

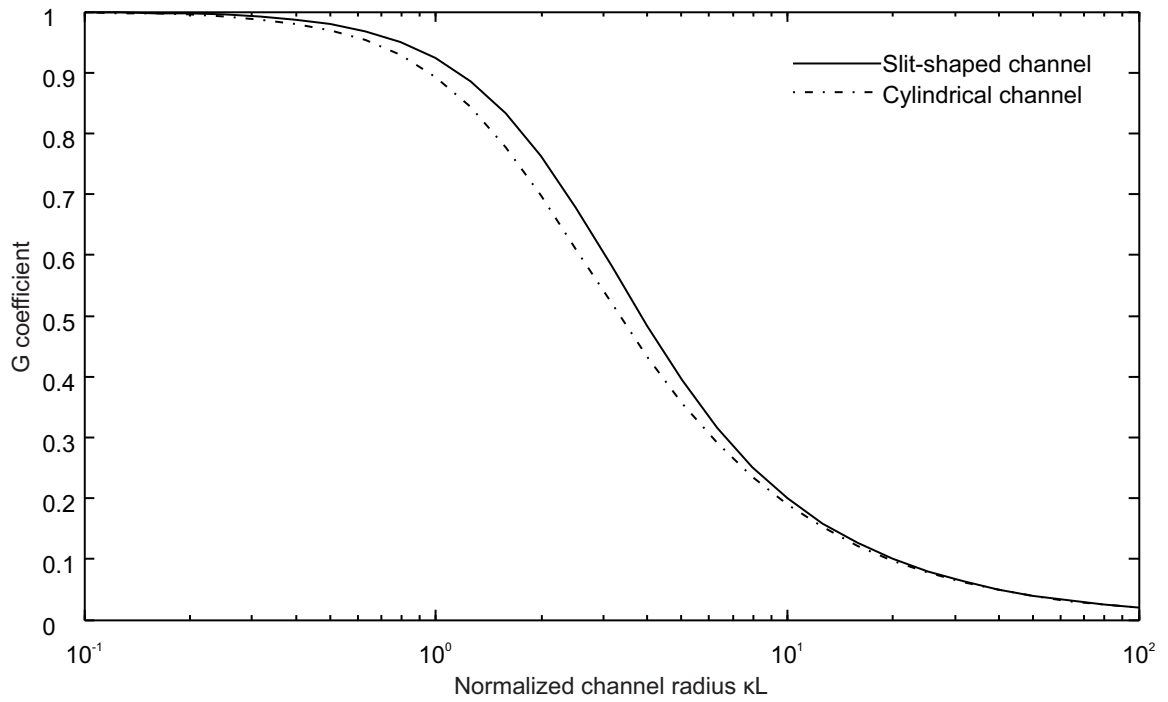


Figure 2.4: Coefficient G versus the normalized EDL thickness for slit-shaped channels and cylindrical channel. L is the characteristic length of the channels, which is the channel height for slit-shaped channels or channel radius for cylindrical channels.

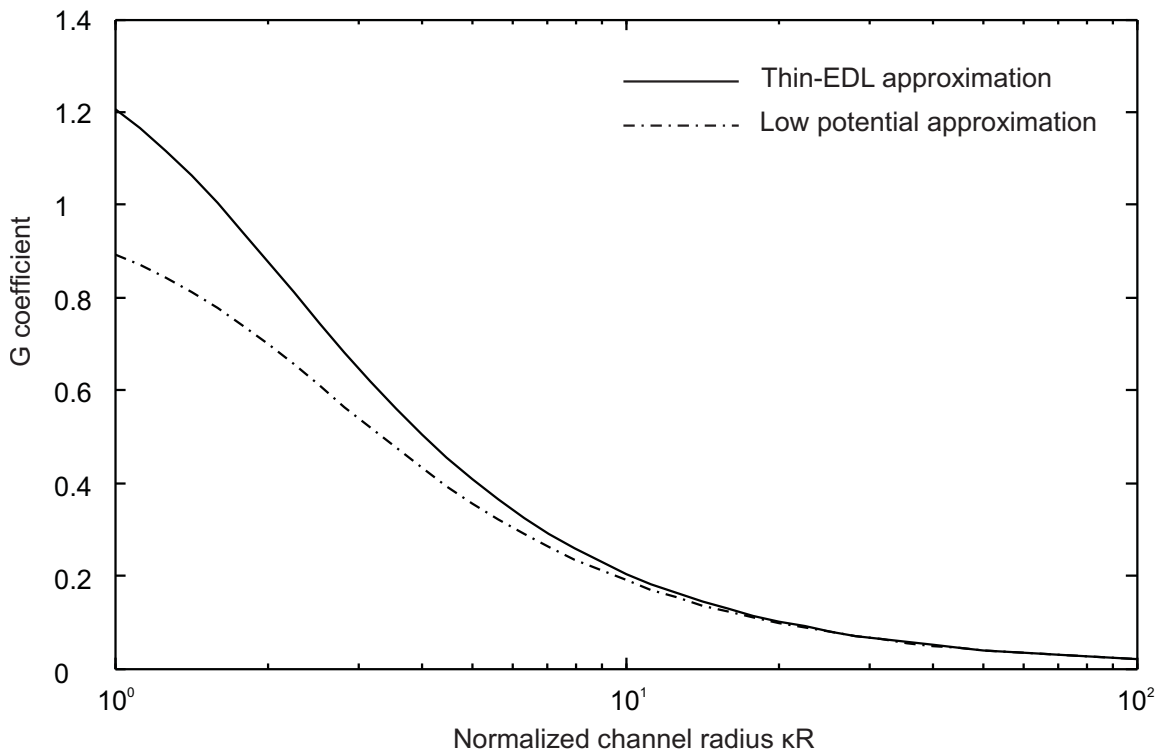


Figure 2.5: Coefficient G versus the normalized EDL thickness for cylindrical channel using thin-EDL and low-potential approximations.

plugs in a hydrophilic nanochannel can be under a negative pressure due to tensile capillary force. Tas et al. [35] investigated the capillary filling speed of water and sodium chloride (NaCl) in nanochannels with rectangular cross section and a height on the order of 100 nm. Their experimental results showed that the filling distance follows Washburn's model, but the filling speed is lower than expected. Han et al. [36] investigated the filling kinetics of different liquids in nanochannels with rectangular cross-section by capillary force. The results again confirmed Washburn's model for capillary filling. Trapping of air bubbles during the filling process was observed. The authors suggested that nanochannels should be used as an idealized model to study mass transport mechanism in systems where surface phenomena dominate. Huang et al. [37] reported a theoretical and numerical investigation on the capillary flows inside microchannels with patterned-surfaces. The equivalent contact angle model for small capillary number flows was introduced and was confirmed by numerical results.

Van Honschoten et al. [38] suggested a model of elastocapillary filling for deformable channels, as shown in Fig. 2.6. In this model, during the filling process, a nanochannel is easily deformed due to the high negative pressure across the meniscus. The model points out that in the elastocapillary filling process, two opposite effects compete: the decreasing channel cross section increases the flow resistance while the Laplace pressure that acts as the driving force becomes more negative due to the increasing meniscus curvature. It was also concluded that the filling speed follows Washburn's model. Mortensen and Kristensen [9] theoretically investigated the electroviscous effect in capillary filling in nanochannels. The theory was established based on the linear relationships among the liquid flow rate, the electric current, the pressure drop and the voltage drop. It was found that the apparent viscosity reaches a maximum in the mesoscopic regime where the hydraulic radius is comparable to the screening length. However, a comparison between theory and experimental data showed that the electroviscous effect contributes just a part to the overall increase of the viscosity.

Nanochannels for capillary filling experiments were fabricated in different materials. Jeong et al. [39] reported a simple method using hydrophilic poly(ethylene glycol) (PEG) to fabricate micro/nanochannels. The capillary filling experiment was performed in PEG-based microchannels to compare with that in hydrophobic polydimethylsiloxane (PDMS)-

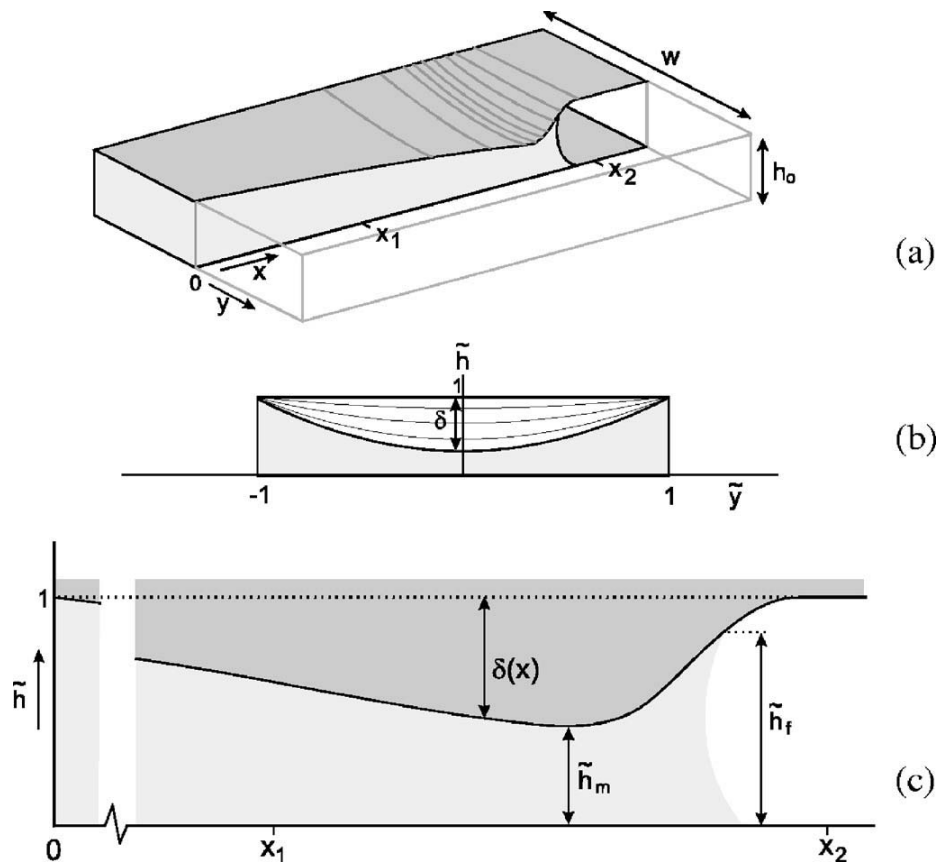


Figure 2.6: Model presented by Van Honschoten et al. for elastocapillary filling in deformable nanochannels: (a) 3D image shows the channel width w and the channel height h_0 ; (b) Cross-sectional area of the channel with normalized channel height $\tilde{h} = h/h_0$ and normalized coordinate $\tilde{y} = 2y/w$; (c) longitudinal view with $\delta(x)$ is the normalized deflection, $\tilde{h}_m$ is the minimum channel height, and $\tilde{h}_f$ is the channel height at the front surface, all the values are determined at $y = 0$. (Reproduced from van Honschoten et al., 2007)

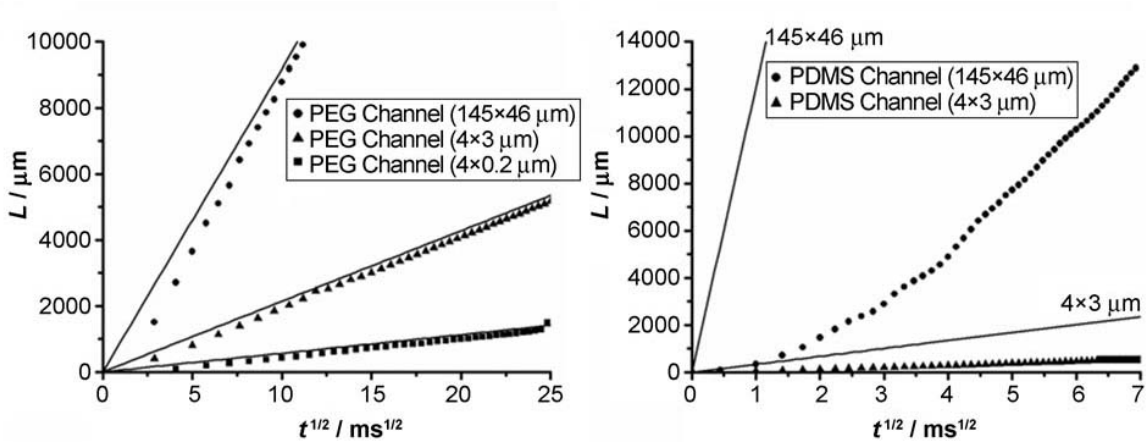


Figure 2.7: Experimental results on capillary filling in PEG-based and PDMS-based microchannel. The solid lines represent the theoretical value. (Reproduced from Jeong et al., 2007.)

based microchannels. The results agreed well with the theoretical prediction based on the simple Poiseuille formation for incompressible Newtonian fluids. Figure 2.7 shows the experimental results reproduced from [39]. Lerch and Jacobson [40] presented microfluidic devices with a two dimensional planar format and methods to assist sample transport along both dimensions. The experiment illustrated fluid handling capabilities in a microfluidic device in a planar format. Persson et al. [41] reported the fabrication of SiO_2 nanochannels using double thermal oxidation scheme. The nanochannels have heights ranging from 14 to 300 nm and widths of 2.5 μm , 5 μm and 10 μm . Capillary filling experiments were also performed to test the channels. Data of the apparent viscosities for different substances and channel height were also reported.

Thamdrup et al. [42] reported an experimental result on the formation of bubbles during capillary filling. The experiments were performed with water in SiO_2 slit-shaped nanochannels with heights ranging from 33 nm to 158 nm. It was found that the formation of an isolated pinned bubble causes a short-time reduction of the filling speed and is accompanied by a forward jump of the meniscus. An anticorrelation between the bubble density and the filling speed was found. Figure 2.8 shows experimental results reproduced from [42], including the filling distance versus time, the increase in apparent viscosity and the formation of air bubbles in a nanochannel. Van Delft et al. [43] reported a microfabricated Fabry-Pérot interferometer with nanochannels of various heights between 6 nm and 20 nm

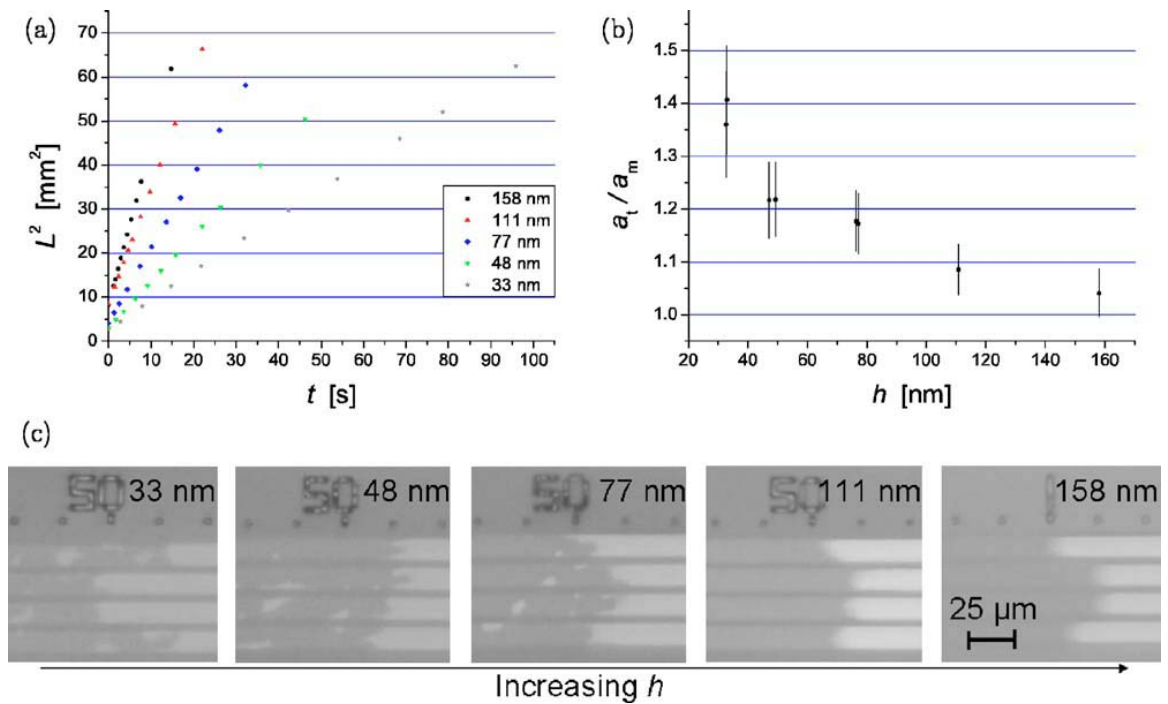


Figure 2.8: Experimental results presented by Thamdrup et al., 2007: (a) Filling distance versus time; (b) Increase in apparent viscosity; (c) Formation of air bubbles during filling process.

embedded in its cavity. This concept allowed the study of fluid behaviour inside a nanochannel without using fluorescent dyes. Capillary filling experiments were carried out in these channels and revealed that the entrapment of air bubble may happen during the filling process. Zimmermann et al. [44] designed a capillary pump for autonomous capillary systems, comprising microstructures of various shapes and dimensions ranging from 15 μ m to 250 μ m. The pumps were designed to have a low flow resistance and are preceded by a constricted microchannel, which acts as a flow resistance. Tas et al. [45] presented a procedure for precise fabrication of silicon-based nanochannels with height ranging from 5 nm to 50 nm using a thin silicon oxide spacer layer. Capillary filling experiments were carried out in these channels. The results showed that the filling process follows Washburn's model with the Washburn coefficient lower than expected with a factor up to 1.6 in nanochannels of 5-nm height. The function of filling distance versus time and the increase in apparent viscosity are presented in Fig. 2.9. Lee and Lee [46] presented the dependence of dynamic contact angle to the movement of a liquid plug in an experimental investigation. Figure 2.10 compares the theoretical investigation [9] and the experimental results of [42, 45]. Devia-

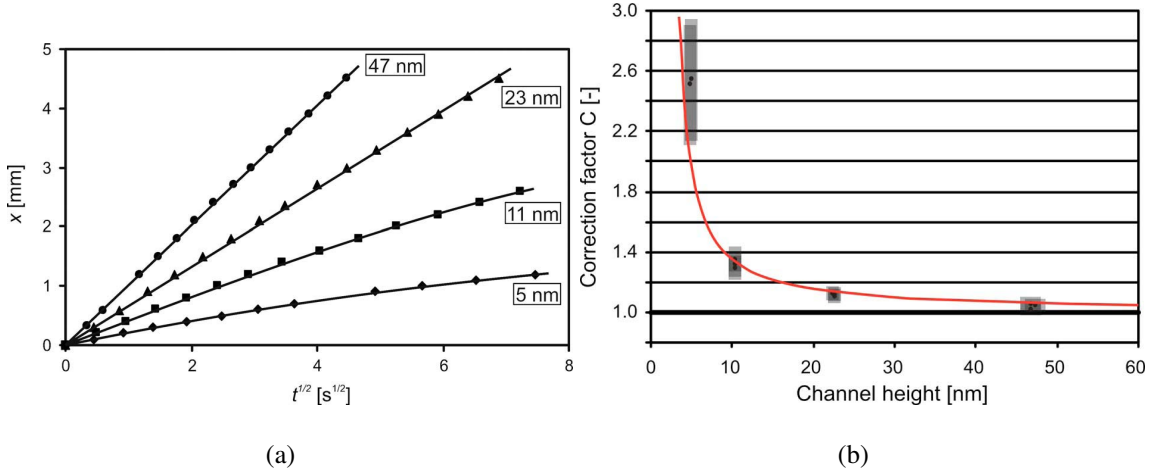


Figure 2.9: Experimental results from Tas et al., 2008. (a) Function of filling distance versus time (b) Increase in apparent viscosity of deionized water in silicon-based nanochannels.

tion between theoretical analysis and experimental results suggested that other phenomena may involve in the change of the capillary filling process of nanochannels.

2.1.4 Pressure Driven Flow

A pressure driven flow in a nanochannel carries with it the electric charge associated with the EDL. The electrically charged particle movement associated with fluid flow is called the streaming current. The streaming current induces an imbalance in electric charge between two ends of the channel. The electric charge imbalance leads to a streaming potential that resists the streaming current. The streaming potential thus induces a conductive current opposing the streaming current. This process reaches the steady state when the streaming current is equal to the conductive current [26, 27]. The process can be described by thermodynamic means as an irreversible process [27, 47, 48]:

$$I = L_{11}\nabla\phi + L_{12}\nabla p \quad (2.15)$$

$$U = L_{21}\nabla\phi + L_{22}\nabla p \quad (2.16)$$

where U is the fluid flow velocity, I is the total electric current, and ∇P and $\nabla\phi$ are the pressure and electric potential gradient acting along the channel. L_{ij} are the Onsager coupling coefficients. The linear assumption requires that the coefficient matrix is symmetric:

$$L_{ij} = L_{ji} . \quad (2.17)$$

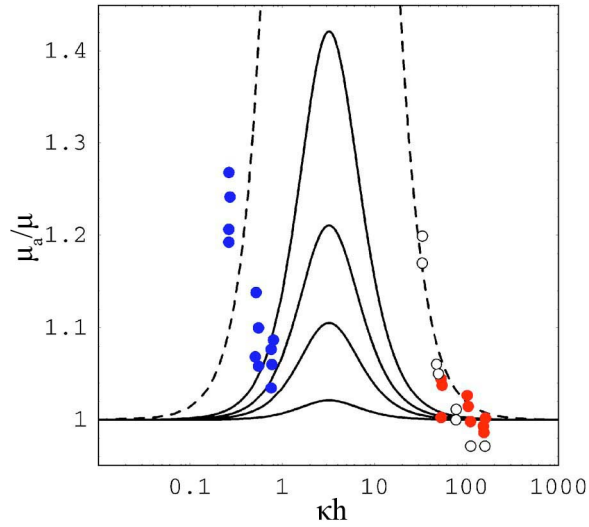


Figure 2.10: Comparison between theoretical investigation by Mortensen and Kristensen, 2008 and the experimental results. Solid lines represent theoretical prediction. White circles show experimental results from Thamdrup et al., 2007. Solid data points show experimental results from Tas et al., 2008. (Reproduced from Mortensen and Kristensen, 2008.)

In steady state, the total current vanishes, Eqs. (2.15) and (2.16) become:

$$0 = L_{11}\nabla\phi + L_{12}\nabla p \quad (2.18)$$

$$U = L_{12}\nabla\phi + L_{22}\nabla p. \quad (2.19)$$

The system above can be solved analytically with the elements of the coefficient matrix which are determined separately [27].

The streaming potential induces a force resisting the fluid flow, on top of the viscous force. This phenomenon is called the electroviscous effect. The effect is greatest for nano-channels that have a characteristic dimension equal to the EDL thickness or slightly larger. The magnitude of the viscosity increases with the zeta potential. It is theoretically estimated that the viscosity increase cannot exceed 30% for slit-shaped channels and 40% for cylindrical channels [27]

2.1.5 Absorption, Evaporation and Condensation

Interactions among gas, liquid, and solid phases in nanoscale play a significant role for many industrial processes [49, 50]. In the past, most of the investigations on nanoscale

transport phenomena were carried out with porous materials. Shaw [51] reported experimental results on the evaporation process in porous materials. This work set a foundation for subsequent works on modelling of the drying process in porous materials. Prat [52] used invasion percolation theory to model the drying processes in porous materials. The model was implemented numerically. Yiotis et al. [53] presented a theoretical model of the drying process in porous materials. This model shows that the formation of a liquid film accelerates the drying process. The model was confirmed experimentally. Recent advances in nanotechnology allow the investigation of liquid transport in deterministic structures such as nanochannels. Experimental results showed discrepancy between liquid transport in nanochannels and those expected in the larger scale. Eijkel et al. [54] showed that film flow and corner flow in nanochannel increase the drying speed of liquid. Capillary filling experiments in open-end channel were conducted by many authors [35,36,42,55]. Most of them reported a lower filling speed than predicted by classical theories. This reduction was explained by different hypotheses. Tas et al. [35] addressed the issue by the electroviscous effect. However, the authors excluded the effect of bubble formation by selecting a filling range where no large bubble formation was observed. Thamdrup et al. [42] observed that the formation of air bubbles further reduces the filling speed. The authors also introduced a correlation between the bubble density and the filling rate. Han et al. [36] performed capillary filling in nanochannels with ethanol, isopropanol, water and mixtures of ethanol and water. The authors explained the reduction in filling rate by the change of dynamic contact angle. Bubble formation was observed in the case of water filling. As described later in Chapter 4, we reported an analytical model for the electroviscous effect in nanochannels [55]. A comparison between this analytical result and experimental results from other authors reveals that the electroviscous effect is not the only cause of the reduction in filling speed. Pesse et al. [56] investigated the capillary filling process in closed-end microchannels. The authors performed filling experiments in rectangular-cross-section, closed-end microchannels with lengths ranging from 50 to 150 μm . Experiments were carried out with deionized water (DIW). Since the first stage of the capillary filling process is relatively fast in microchannels, the authors mainly reported the results of the second stage where trapped air dissolves in water. The time scales of the experiments are several hours to a day. Due to the existing water vapour in air and its condensation under high Laplace

pressure, the filling process does not have a clean meniscus. The experimental data were compared with a simple theory. However, due to the complicated appearance of the meniscus and droplet formation in the trapped air region, the experimental data could not fully fit the theoretical model. In the model suggested by Pesse et al., [56] only absorption and diffusion of air in liquid were considered, due to the relatively low Laplace pressure in microchannels compared to atmospheric pressure. In nanochannels, the Laplace pressure is high enough to cause significant air compression. Therefore, air compression plays an important role in transport of fluid in nanochannels.

2.2 Fabrication, Experiment and Modelling of Nanochannels

Besides the development in theory, many works in fabrication, characterization and simulation of nanochannels have been carried out, especially in recent years. New experimental and numerical results, as well as advances in fabrication techniques allow new phenomena to be explored. Theoretical results can be validated through experiments.

Schasfoort et al. [11] carried out an experiment to control the magnitude and the direction of the electroosmotic flow inside a microfabricated nanochannel by applying a perpendicular electric field. The experiment introduced a microdevice called a “flowFET”, with functionality comparable to that of a field-effect transistor (FET) in microelectronics, and thus illustrating the potential of the flowFET as a controlling and switching element in microfluidic networks. Figure 2.11 shows the working principle of the flowFET.

Mitchell et al. [57] demonstrated the simulation of electroosmosis transport in microsystems. Meshless techniques were used to find numerical solutions of the Laplace equation, the PB equation and the incompressible Stokes or NS equations. The results were presented for a straight channel, a cross-shaped and a T-shaped intersection.

Conlisk et al. [58] examined fluid flow and mass transfer field in a rectangular channel under the influence of electric. The fluid considered was a mixture of water or another neutral solvent and a salt compound for which the ionic species are entirely dissociated. Results showed that at small electrolyte concentrations, the EDL distribution is as predicted

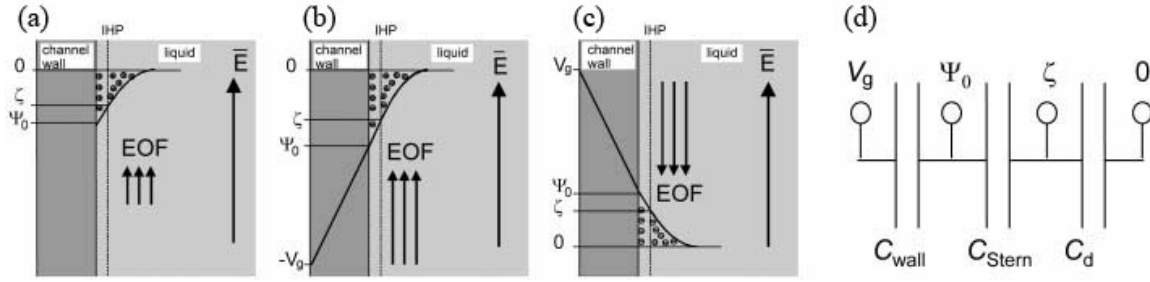


Figure 2.11: Working principle of a flowFET: (a) Electroosmotic flow without control field; (b) Electroosmotic flow with the control field applied; (c) The flow with reversed field; (d) The simplified model of the liquid-solid interface. (Reproduced from Schasfoort et al., 1999.)

by Debye-Hückel model, while at higher concentrations the EDL distribution follows the Gouy-Chapman model. The numerical results confirmed the analytical solution of a singular perturbation analysis, which is valid as the channel height increases. In the symmetric case, the velocity profile has the same form as the potential profile. In the asymmetric case, the two wall potentials are different, leading to discrepancy between velocity profile and potential profile. For an electrically driven flow, the volumetric flow rate is proportional to the channel height. For a pressure driven flow, the volumetric flow rate is proportional to the cube of the height. This scaling relationship showed that in micro- and nanochannels, electrically driving is a more efficient method compared to pressure driving.

Zheng et al. [59] described the effect of multivalent ions on electroosmotic flow incorporating Ca^{2+} and HPO_4^{2-} as well as other monovalent ions, such as K^+ and H_2PO_4^- , into an aqueous NaCl solution. A numerical solution was derived for this case. The authors found that in micro- and nanochannels with fixed surface charges, multivalent counterions, even in very small amounts, reduce the electroosmotic flow significantly, while the multivalent co-ions have little effect on the electroosmotic flow. This effect was explained by the majority of counterions in the composition of the Debye layer.

Ejikel et al. [60] performed spontaneous filling of nanochannels with water, ethanol and isopropanol, as well as electroosmotic flow in nanochannels with heights of 100 nm and 500 nm. The nanochannels were made of polyimide, which has good electrical and mechanical properties and is biocompatible. Fabrication steps and the image of final product are shown in Fig. 2.12.

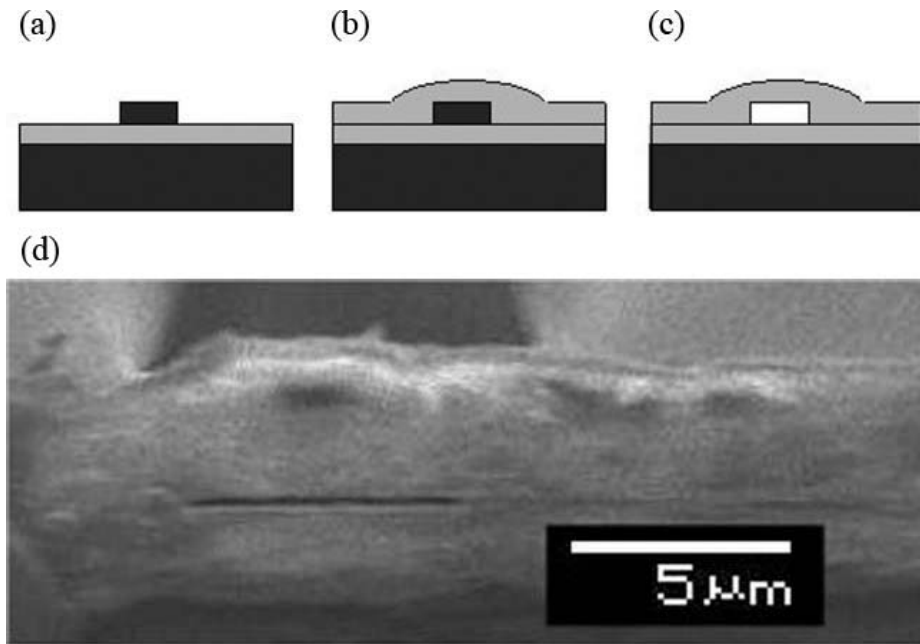


Figure 2.12: Fabrication steps of a polyimide-based nanochannel: (a) A layer of polyimide was spin-deposited on a silicon wafer, aluminium was deposited on top then patterned; (b) Another layer of polyimide was spin deposited and photo patterned; (c) Aluminium was removed by wet etching to form the nanochannel; (d) Cross-sectional image of a channel with 100 nm height and 5 μm width. (Reproduced from Ejikel et al., 2004.)

Kirby and Hasselbrink [61] presented the theoretical and measured results of the zeta potential of several materials depending on cation concentration, buffer, cation type, pH, cation valency and temperature. The results showed that the Debye-Hückel approximation (low-potential approximation) can lead to serious error if being used to determine the relation between zeta potential and the counterion concentration. For silica substrate, experimental measurements showed that the high-zeta-potential limit of the PB equation is most applicable. Therefore, the zeta potential on silica substrate is approximately proportional to the logarithm of the molar counterion concentration. The zeta potential versus pH relation was also derived experimentally by normalizing the zeta potential based on the concentration. For polymeric substrate materials, normalizing zeta potential by pC (concentration level) was suggested. Although the available data was not sufficient to obtain a complete and rigorous conclusion, it was observed that the experimental data agrees well with double layer and absorption theory.

Pu et al. [62] announced a new phenomenon found in nanostructures: the ion enrichment/depletion under effects of an applied voltage. Due to the overlapping of the EDL,

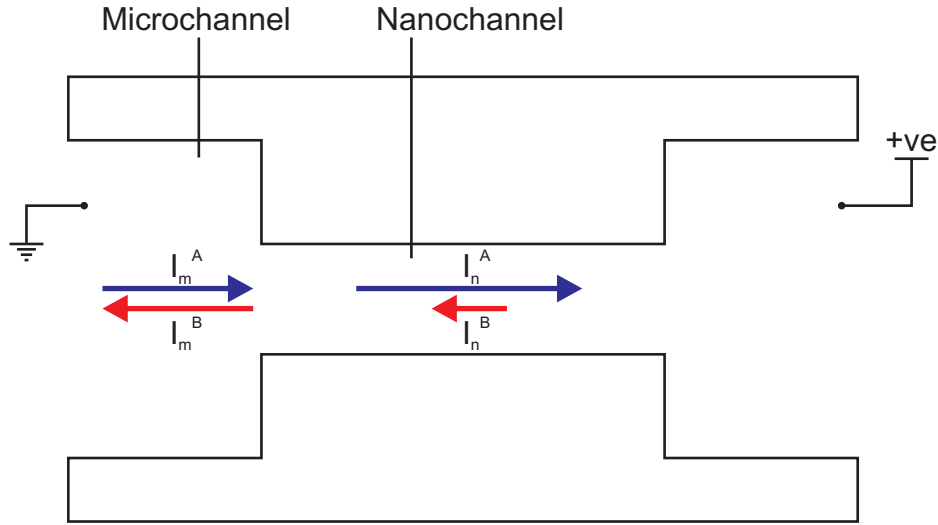


Figure 2.13: The ion enrichment/depletion under effects of an applied voltage. I_m^A is anion drift current in microchannel, I_n^A is anion drift current in nanochannel, I_m^B is cation drift current in microchannel, I_n^B is anion drift current in nanochannel

the concentrations of ions in the nanochannel are different from those in bulk reservoirs or microchannels. The drift motion of ions is proportional to the ion concentration. Applying Kirchhoff's circuit law to the regions inside and outside of the nanochannel, the enrichment/depletion rate of ions near the nanochannel entrances was formulated. The ion enrichment/depletion effect is shown in Fig. 2.13.

Sadr et al. [63] performed an experiment on fully developed and steady electro-osmotic flow in a rectangular channel where the channel height is comparable to its width and much higher than the EDL thickness. Two components of the velocity field were measured by nanoparticle image velocimetry. The results were within 10% of analytical prediction for mobility over a 200-fold change in concentration values.

Bhattacharyya et al. [14] used numerical method to analyse the electroosmotic flow in a rectangular channel with an aspect ratio on the order of unity. The condition of simulation is the same as reported by Conlisk [58]. Numerical solutions were provided for both symmetric and asymmetric velocity, potential and mole fraction. Results were derived for both cases with a channel height much greater than the EDL thickness and with a channel height at the same scale as the EDL thickness. It was shown that the Debye length is not a good measure of the actual thickness of the EDL. Results for binary electrolytes agree well with the experimental data. Asymptotic solution was provided for the case of three-component

mixtures.

With the same assumption as in [58], Conlisk [64] reported the analysis of electroosmotic flow in a rectangular channel, where the height is much larger than the EDL thickness. The results showed that at small differences of ion concentration, the Debye-Hückel approximation is appropriate. At a higher concentration difference, the Gouy-Chapman model of the EDL is appropriate. The limits of the Debye-Hückel approximation were also reported. The relationship between the concentration of the electrolytes at the wall and the zeta potential was also derived. In this model, continuum assumption was adopted.

Eijkel and van den Berg [65] proposed the term “water potential” which is convenient for describing the energy level of water at different points in a system. The water potential is useful to determine the direction of flow in the system under the influence of either capillary, gravitational or electric force.

Mela et al. [66] reported the measurement of zeta potential of cyclo-olefin polymer surface as a function of pH, counter-ion concentration, storage conditions, and chemical treatment in aqueous solutions both with and without EOF-suppressing additives. Significant surface charges were measured, which contrasted the results of previous reports. The results also showed that the storage condition only has minor effects.

Nath et al. [67] introduced a system for flow measurement in micro/nano fluidic components. The measurement was performed by arrays of straight microchannels with non-circular cross-sections. Finite difference approximation method was used to determine the flow rate. The results were confirmed in an experiment, where the flow rates were measured by collecting the fluids on a sensitive balance while the pressure was controlled by a pump system. The investigation showed that the flow rates calculated by the finite difference approximation method were within 5.50% and 19.7% of the average experimental flow rates in the microchannels and nanochannels, respectively.

Van der Heyden et al. [68] reported measurements of the streaming current in individual rectangular silica nanochannels down to 70 nm in height. It was found that the results are best modelled using a non-linear PB theory that includes the salt-dependent hydration state of the silica surface. Firstly, streaming current is proportional to the pressure gradient and increases with the channel height. Secondly, streaming current is approximately constant at concentration below 10 mM, whereas it strongly decreases at higher salt concentration.

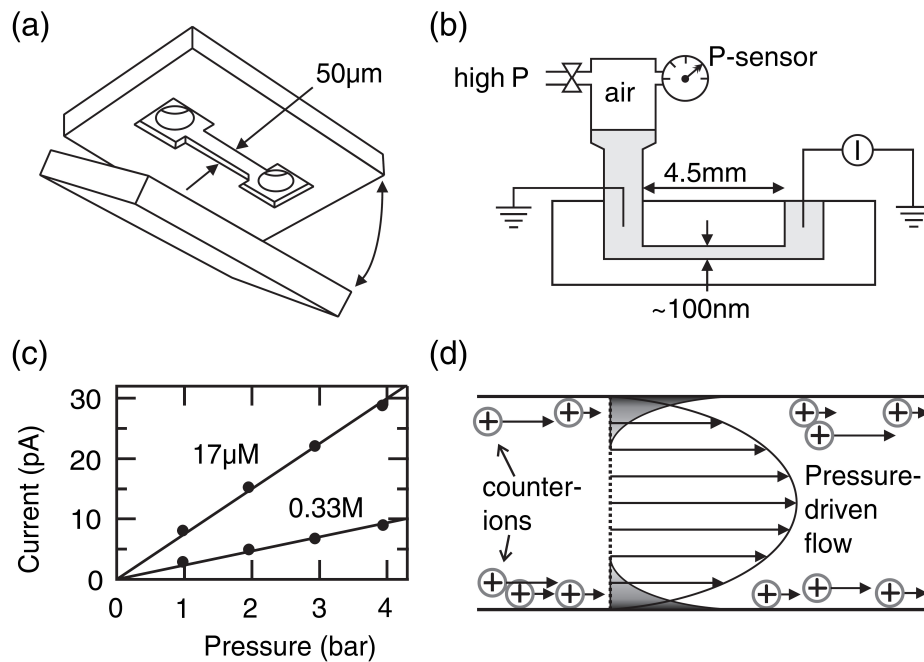


Figure 2.14: Experimental setup to measure streaming current: (a) Chip design with nano-channel; (b) Equipments setup; (c) Graph of streaming current versus driving pressure; (d) The velocity profile in channel. (Reproduced from Van der Heyden et al., 2005.)

And lastly, changing the sign of the surface charge reverses the streaming current. Figure 2.14 presents the experimental setup used by the authors to determine the streaming current and streaming conductance. The authors also suggested applications of streaming current in energy conversion [69–71]. In [71], the authors carried out an experiment on the efficiency of electrical power generation in individual rectangular nanochannels by means of streaming currents. The efficiency was considered as a function of the channel height and salt concentration. It was showed that the highest efficiency occurs when the EDLs overlap, which corresponds to a nanochannel filled with solutions of low ionic strength.

Non-equilibrium molecular dynamics simulations were used by Zhu [72] to investigate the electroosmotic flow. It was found that although hydrodynamic theory adequately describes simple pressure-driven (Poiseuille) flow, PB theory fails to describe the ion distribution in important situations, and therefore continuum fluid dynamics based on the PB ion distribution disagrees with simulation results in those situations. The failure was explained by the exclusion of ions near the channel walls resulting from reduced solvation of the ions in that region. A corrected ion distribution was also introduced to fit analytical and numerical results.

Gao et al. [73] reported a theoretical investigation of the pressure-driven two-liquid flow in microchannels with electroosmotic effect. The investigation provided an analytical solution relating the velocity profiles and the flow rates to the liquid hold-up, the aspect ratio of the microchannel, the viscosity ratio of the two liquids and the externally applied electric field. The investigation considered the combined effect of pressure difference and electroosmotic force on a steady state, laminar two-liquids flow.

Hug et al. [74] performed spontaneous filling with aqueous, florescent solution in nano-channels of 1-mm long and 200-nm width and height and microchannels of 20- μm width and 4.8- μm height. The channel is made of silicon dioxide. The external electric field of 600 V/cm is created in the channel by applying a voltage of 10 V. The electroosmotic flow through the micro- and nanochannel was measured.

Leinweber et al. [75] introduced the concept of continuous flow demixing of electrolytes by using structured electrode arrays. In this investigation, the axial electric potential gradients induced lateral molecular transport via a system of a large number of electrodes. A solution of electrolyte with homogeneous concentration can be demixed to regions with different concentrations using this method.

Mahabadi et al. [76] reported the fabrication of poly(methyl methacrylate) (PMMA) microfluidic channels by proton beam writing. High-molecular-weight PMMA was used. Channels with 200 nm width was fabricated, the smoothness of the channel wall was measured down to 2.45 nm. The channels were sealed by thermal bonding. Current monitoring was used to derive the electrokinetic properties. Electroosmotic flow profile was also investigated by particle image velocimetry. A theoretical model was developed to predict the bulk electroosmotic flow of phosphate buffer solution in PMMA microchannels and this model showed good agreement with the measured electroosmotic mobilities. The images of fabricated channels are shown in Fig. 2.15.

Qiao et al. reported a series of simulation works on the transport of ions through nanostructures [77–83]. The simulations were performed with nanochannels, carbon nanotubes, and heterogeneous osmosis membranes. The results revealed some differences between numerical and analytical approaches.

Qiao and Aluru [79] showed that the continuum assumption may introduce error to the simulated flow in carbon nanotube. The relationship between electroosmotic transport

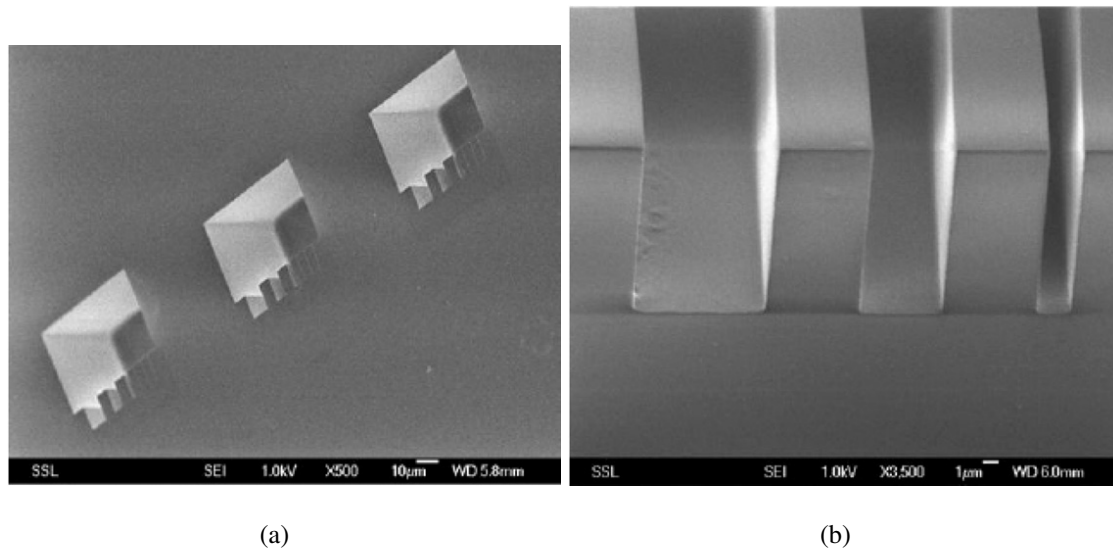


Figure 2.15: Scanning electron micrograph (SEM) of microfluidic channels produced by proton beam writing: (a) The channels connected to $10\text{-}\mu\text{m}^2$ reservoirs; (b) Close view shows the channels with the depth of $60\text{ }\mu\text{m}$ and the height ranging from 400 nm to $10\text{ }\mu\text{m}$. (Reproduced from Mahabadi et al., 2006.)

and the surface charge is mainly caused by the different adsorption behaviour of the counterions, which depends on the size of the counterion, the local electrostatic interactions between ion-water and ion-charged surface atoms, and on the external electric field.

A new approach for controlling turn-induced dispersion in nanofluidic channels was introduced by Qiao and Aluru [78] based on the local control of zeta potential. The authors built an algorithm to find the optimal configuration for the zeta potential. The results showed that the dispersion can be lowered significantly.

Electroosmotic flow in nanochannels with widths ranging from 0.95 to 10 nm was investigated by the same authors in [77]. Molecular dynamics (MD) and continuum simulations were used. The simulation results for various cases showed that finite size of the ions and the discreteness of the solvent molecules affect the ion distribution in the channel significantly.

Charge inversion and flow reversal of electroosmotic transport in a slit-shaped silicon nanochannel was investigated in [80] using MD simulations. It was found that the charge inversion is mainly caused by the molecular nature of water and ions and the flow reversal is caused by the immobilization of counterions adsorbed on the channel wall and due to the charge inversion phenomena.

The scaling of electroosmotic flow and ionic conductivity in positively charged slit nanochannels was discussed in [82] using continuum and atomistic simulations. The results showed that the viscosity of the interfacial water increases substantially as the surface charge density increases and the electrophoretic mobility of the interfacial ions decreases. The effects were found to influence the scaling of the electrokinetic transport in confined nanochannels significantly.

In [81], the ion distribution and velocity profiles of KCl solution in two oppositely charged silicon nanochannels were analysed using MD simulations. It was found that the counter-ion distributions are substantially different in the two channels. Moreover, the water flux and ionic conductivity in the two channels differ by a factor of more than three. These results are not expected by continuum theory. The discrepancy may be caused by the different sizes of the K^+ and Cl^- ions, the discreteness of the water molecules, and the asymmetric dependence of the hydrogen bonding of water near the charged silicon surface.

Using MD simulations, water and ion transport through a heterogeneous membrane separating two electrolyte solutions at different concentrations was investigated by Qiao et al. [83]. Simulation results showed that the differential transport of K^+ and Cl^- ions through the membrane pores creates an electrical potential difference across the membrane, which then induces an electroosmotic water flux.

Ramirez and Conlisk [84] carried out computational fluid dynamics simulations of electroosmotic flow in nanochannels and examine the effects of sudden changes in channel cross-section area. The formation of vortices or recirculation regions near the step face was observed when the width of the EDL is large enough. Figure 2.16 shows the vortices forming at the step face in the case of large EDL, in comparison to the case of thin EDL.

Schoch [85] investigated transport phenomena in microfabricated nanochannels. From this study, fundamental nanofluidic ionic transport in nanochannel was analysed, forming a basis for novel separation and preconcentration applications.

Conlisk et al. [86] analysed both steady-state and transient electroosmotic flow for two and three ionic components in a nanochannel. Numerical solution was considered. Short transient regime can be achieved by a sudden introduction of a species at the inlet of the channel. Steady-state electroosmotic flow is established when all important parameters such as concentration, potential, and velocity are independent of the stream wise coordi-

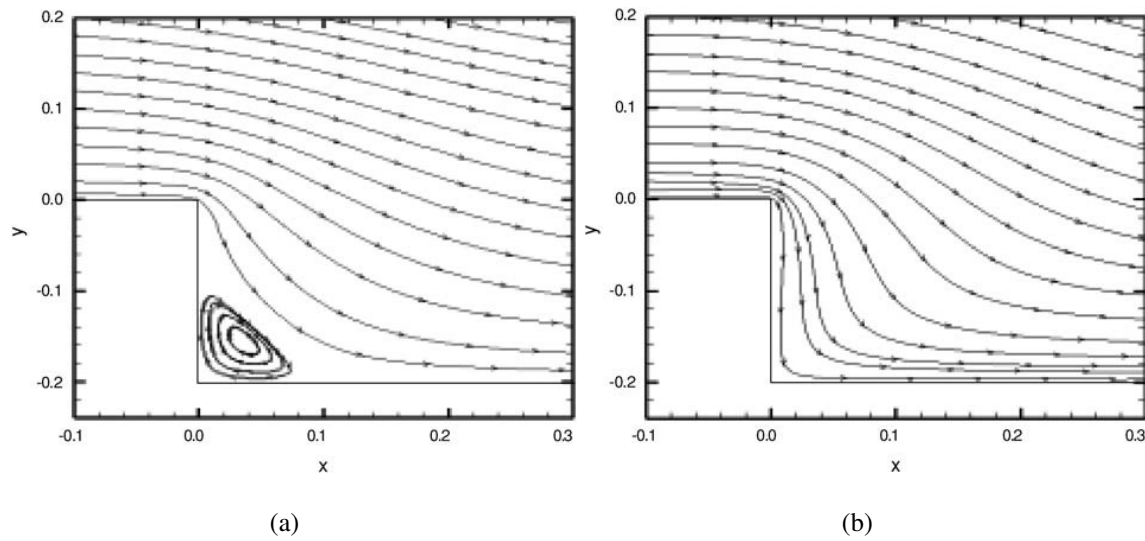


Figure 2.16: Electroosmotic flow in channels with the step face along the flow. The heights of channels are 50 nm upstream and 50 nm down stream. The electric field is induced by a voltage of 6 V applied along the channel length of 3.5 μm : (a) Vortices form at the step face in the case of overlap EDL; (b) Flow stream without vortices in the case of thin EDL. (Reproduced from Ramirez and Conlisk, 2006.)

nate. Direction of the movement of species is governed by the Fickian diffusion, electrophoresis phenomena and bulk convection. The results showed that on the one hand in channels with negatively charged walls, a negatively charged species may move in opposite direction of those of the bulk fluid flow. On the other hand, a positively charged species is transported in the direction of fluid flow and there is a significant decrease in the transit time as compared to an uncharged or negatively charged species. The formulae for the concentration and species flux were derived. The comparison between steady-state model and experimental results showed a very good agreement.

Lerch and Jacobson [40] used SIMION and COMSOL to model the electric fields and fluid flow in the microfluidic devices with a two-dimensional planar format. The design consisted of a single channel for the first dimension which orthogonally intersected a high-aspect-ratio second-dimension channel. Control channels were placed on both sides of the first-dimension channel to reduce dispersion in the second-dimension flow. Several designs were fabricated and tested. The results showed that the design with four control channels provided the most effective sample confinement. It was also showed that multiple parallel channels in second dimension improve the performance of the device.

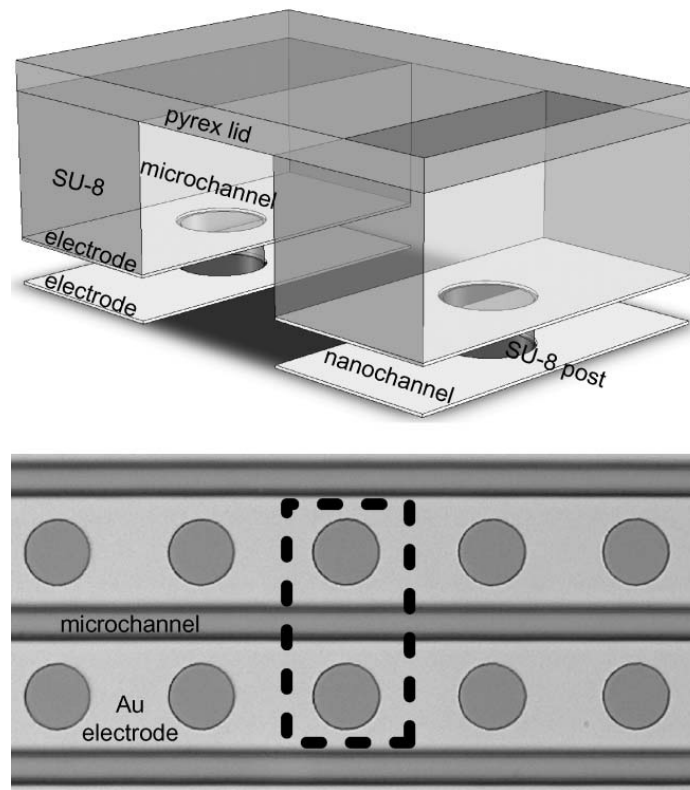


Figure 2.17: A typical design for channel fabrication using sacrificial etching. The bottom image shows the top view of the chip. Circular opening in the aluminium electrode allows SU-8 to support the nanochannels. The top image shows 3D image of the dashed box drawn in the bottom image. (Reproduced from Nichols et al., 2007.)

Nichols et al. [87] presented sacrificially etched 2-D nanofluidic channels and nanospaces with integrated floor and ceiling electrodes and arbitrary channel geometries. SU-8 was used as the structural material. A typical design of the channels is presented in Fig. 2.17. The channels were fabricated with channel heights ranging from 20 nm to 400 nm, channel widths from 800 nm to 40 μm , and lengths up to 3 mm.

Ogawa et al. [88] reported the fabrication of tilted and square distributions of nanopillars, as shown in Fig. 2.18. Nickel plating was performed by applying a stable electric current. Experiment of DNA separation in this nanopillars pattern showed that with tilted distribution, the DNA showed reptile movement and DNA separation can be achieved. In contrast, with a square distribution, DNA molecules showed straight movement and DNA did not separate. However, conformation change of DNA in square distribution pattern was observed. It was concluded that reptile movement is an important factor for DNA separation.

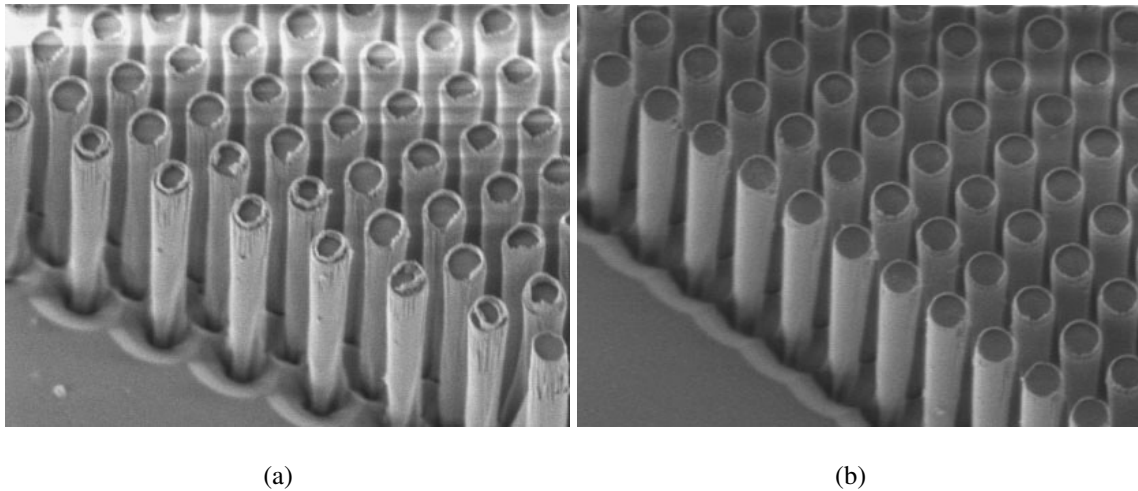


Figure 2.18: Quartz nanopillars patterns with a distance between pillars of 300 nm and a pillar height of 4 μm : (a) Tilted distribution, in which the DNA showed reptile movement; (b) Square distribution, where the DNA showed straight movement. (Reproduced from Ogawa et al., 2007.)

Pennathur et al. [89] presented an experimental investigation of electrokinetic transport and separation of double-stranded DNA oligonucleotides in custom-fabricated fused-silica nanochannels filled with a gel-free sodium borate aqueous buffer. It was found that oligonucleotide migration time depends on both the ratio of length of DNA molecules to channel depth, and the ratio of channel length to its depth. At background electrolyte concentrations of 1 and 5 mM, the measured electrophoretic mobility was higher than previously published values. The highest separation sensitivities were achieved in 100 nm channels with 1-10 mM ion density buffers.

Persson et al. [41] presented a double thermal oxidation scheme for fluidic systems with silicon dioxide nanochannels with heights ranging from 14 to 300 nm and widths of 2.5, 5 and 10 μm . The technique is based on the growth of silicon dioxide, ultraviolet (UV) lithography, etching, and fusion bonding. The technique showed improvements with respect to 4-inch wafer height variation and low surface roughness. The capillary filling speed in different channel heights ranging from 14 nm to 310 nm was measured. The experiment repeated and extended the results reported by Tas et al. [35].

Plečis and Chen [90] described an alternative technology for the fabrication of microfluidic devices using a glass-PDMS-glass sandwich configuration. The technique uses a patterned PDMS layer as both a bonding layer and a working layer for lateral fluid con-

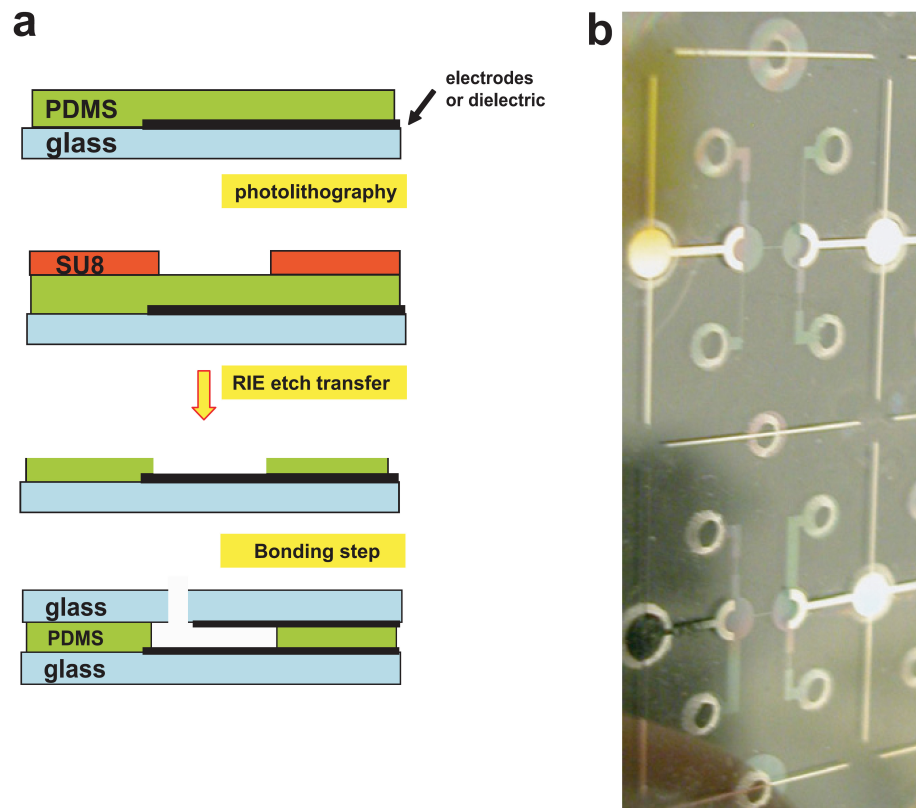


Figure 2.19: PDMS-based microfluidic device. (a) Fabrication steps (b) Image of final product. (Reproduced from Plecis and Chen, 2007.)

finements. The devices were tested by measuring the electroosmotic flows in microfluidic channels coated with different materials. The fabrication steps and image of the final product are shown in Fig. 2.19.

Kusumaatmaja et al. [91] reported the effect of posts or ridges on the sides of the microchannels on capillary filling. The results showed that ridges perpendicular to the flow direction slow down filling, whereas ridges parallel to the flow may enhance filling.

Hong et al. [92] applied numerical methods to investigate the dynamic contact angle of water droplet moving on a solid surface. It is observed that under the presence of a body force, the contact angle of the droplet may change. During the droplet motion the advancing contact angle is larger than the receding contact angle. If the principle is also valid in the filling process in a nanochannel, the change in dynamic contact angles affects the capillary force, therefore, changes the filling speed of liquid.

Zhang et al. [93] investigated the negative pressure across the meniscus of water flows in nanochannels by numerical simulation. The probability of cavitation formation due to

this negative pressure was calculated. The results showed that cavitation does not occur in nanochannels of uniform cross section because the critical diameter of such cavitation is larger than the size of the channels. However, the cavitation may happen in channels with non-uniform cross section. This result is based on planar nanochannels but can be generalized to elliptical or circular cross section nanochannels. However, it is worthy to note that this investigation only focused on the formation of cavitation in the fluid due to low pressure, not on the bubbles captured by irregular movement of the meniscus.

Chapter 3

Fabrication of Nanochannels

3.1 Background

There are many approaches in fabrication of nanochannels with cap layer. Each of them has specific advantages and disadvantages. Some offer excellent mechanical properties while others promise great applications with their flexibility. These approaches were discussed in the perspective article by Abgral and Nguyen [7]. Figure 3.1 briefly introduces several main approaches in fabrication of nanochannels. This figure is only for illustration purpose and does not aim to provide a detailed review.

The main objective of our fabrication work is to prepare a platform for subsequent experiments. However, the author also explored improvements in fabrication of polymeric nanochannels. Traditionally, silicon nanochannels are preferred for experiments. The techniques to manipulate silicon material are well-developed. Silicon also offers excellent chemical and mechanical properties. Nanochannels made of silicon can reach to a very high resolution and precision.

Preliminary design and fabrication jobs were done in the Thermal and Fluid Research Laboratory, Nanyang Technological University (NTU), Singapore and Centre for IC Design and Nanofabrication, Singapore Polytechnic (SP), Singapore. The closed-end nanochannels used in Chapter 5 were fabricated by CNRS Laboratoire d'Analyse et d'Architecture des Systèmes (LAAS), France, using a similar technique. The fabrication process, as well as subsequent experimental results, was published in [94, 95].

Polymer emerges in recent years as a flexible platform to fabricate nanochannels. Overcoming the disadvantage in properties of the material, such as low hardness or relatively low melting point, the techniques to manipulate polymeric material in nanoscale advance quickly recently, making it possible to fabricate polymeric nanochannels with decent accuracy [96]. In this thesis, the author explored the optimum conditions to fabricate nanochannels by hot embossing and thermal bonding with polymethyl-methacrylate (PMMA). The silicon molds for hot embossing were designed in Nanyang Technological University by Dr. Patrick Abgral and were fabricated at Centre for IC Design and Nanofabrication, SP. The hot embossing and thermal bonding were performed at Thermal and Fluid Research Laboratory, NTU and Centre for Ion Beam Applications, National University of Singapore (NUS), Singapore. Atomic force microscopic analyses of the molds and the nanochannels were performed at Precision Engineering and Nanotechnology Centre, NTU.

3.2 Fabrication of Silicon Nanochannels

3.2.1 Materials and Method

Figure 3.2 shows the fabrication process of planar nanochannels in silicon. The process started with RCA (Radio Corporation of America) cleaning of the wafer, Fig. 3.2(a). This cleaning process consisted of three steps. The first step removed insoluble organic contaminants with a 5:1:1 $\text{H}_2\text{O}:\text{H}_2\text{O}_2:\text{NH}_4\text{OH}$ solution. The second step removed the thin silicon dioxide layer using a diluted 50:1 $\text{H}_2\text{O}:\text{HF}$ solution. The third step removed ionic and heavy metal contaminants using a solution of 6:1:1 $\text{H}_2\text{O}:\text{H}_2\text{O}_2:\text{HCl}$.

Following the cleaning step, photolithography was used to define the pattern of the nanochannels on a photoresist film (AZ 1512), Fig. 3.2(b). The photoresist was spin-coated in two steps, 500 rpm for 20 seconds and subsequently 2000 rpm for 10 seconds. The resist was then soft-baked at 90°C for 2 minutes. After the UV exposure, the resist was developed by a mixture of a volume ratio of 2:1 of AZ Developer and DIW for 20 seconds. The wafer was subsequently rinsed with DIW for 1 minute and dried with nitrogen. In the last stage, the resist was hard-baked at 120°C for 2 minutes. A resist layer of about 1 μm was confirmed by the measurement with an optical profiler.

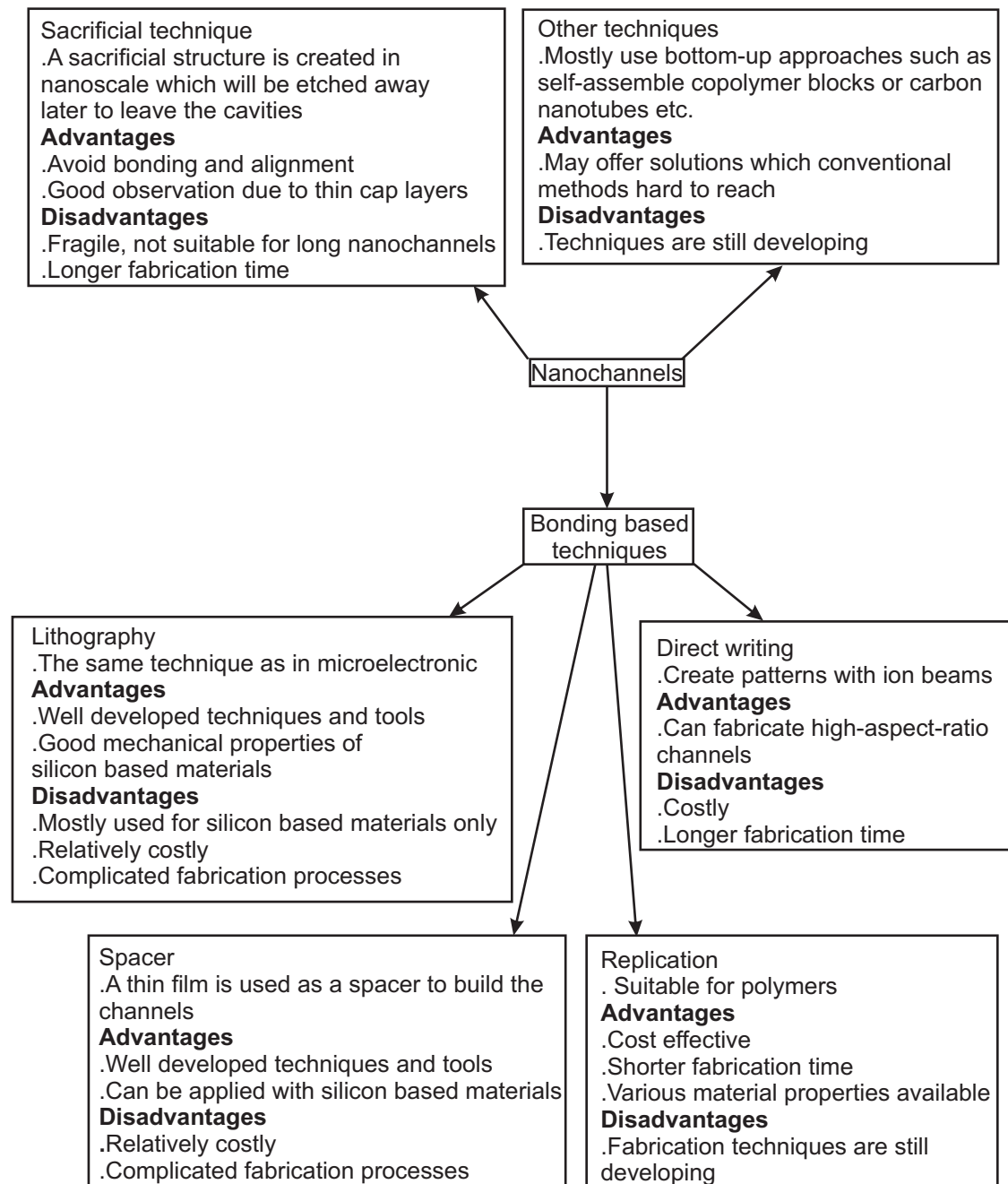


Figure 3.1: Summary of different approaches in fabrication of nanochannels.

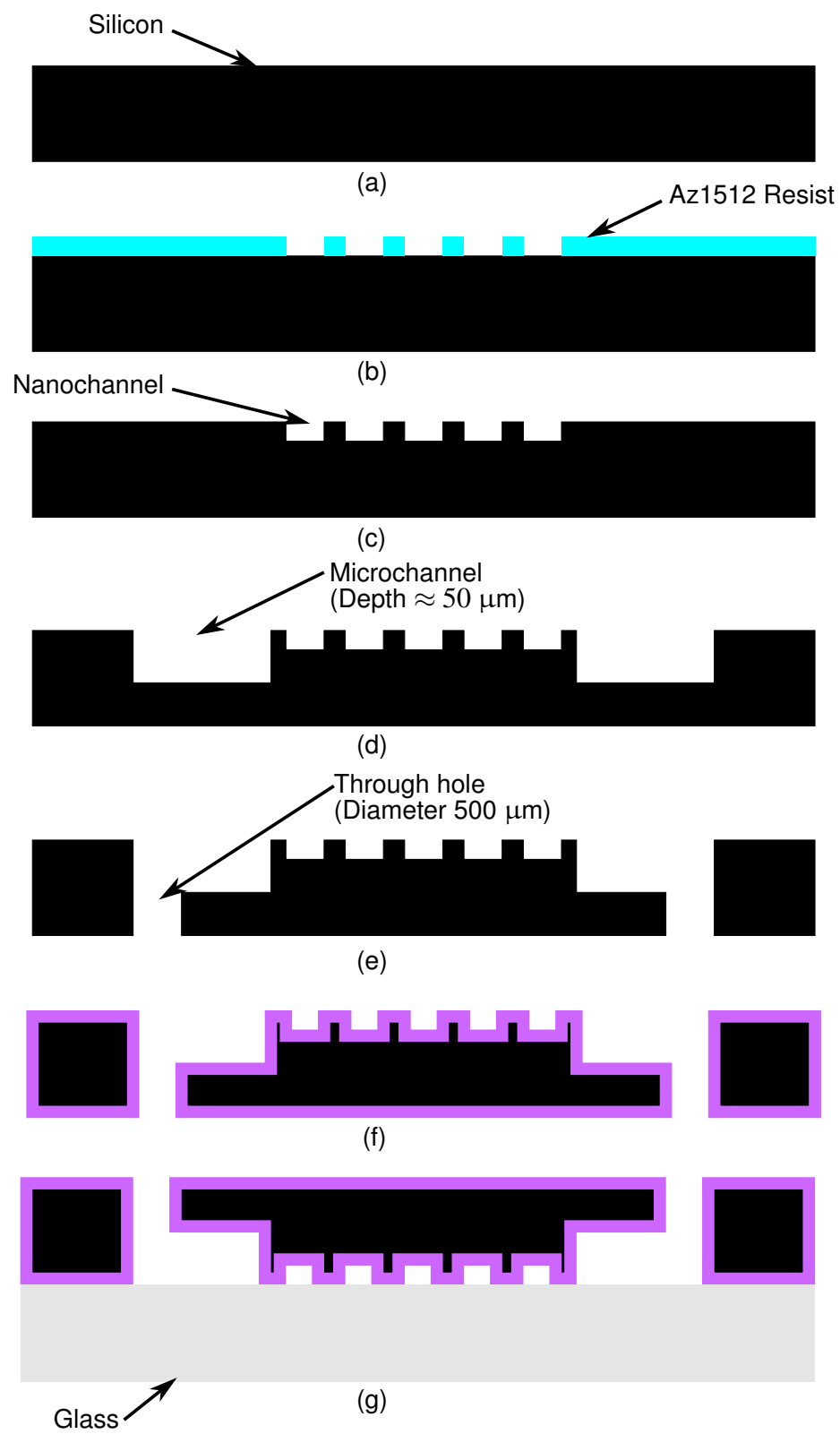


Figure 3.2: Fabrication steps of a planar nanochannel in silicon and glass

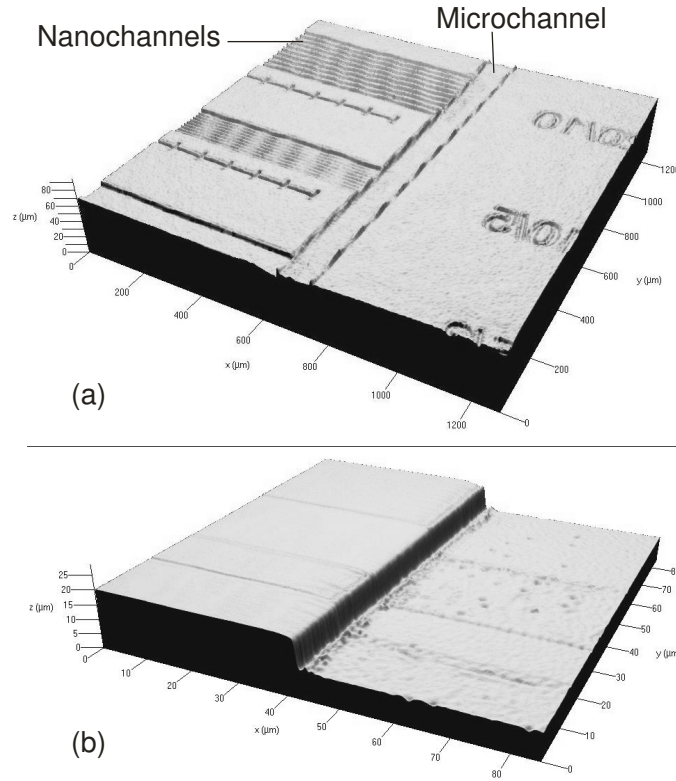


Figure 3.3: The fabricated device: (a) Nanochannel array with a microchannel at the inlet; (b) Details at the wall of the microchannel.

Using the patterned photo resist as a mask, nanochannels with a depth of 40 nm to 200 nm were etched at a pressure of 4.0 Pa, 30 sccm CF_4 , 5 sccm O_2 , a power of 300 W, Fig. 3.2(c). The average etching rate with this recipe was 0.564 nm/sec. The photoresist was removed by oxygen plasma. Before proceeding to the next step, the wafer was baked at 120°C for 30 minutes.

A second photolithography step protected the nanochannels with the photoresist and formed the mask for deep reactive ion etching (DRIE) of the 50- μm deep microchannels, Fig. 3.2(d). The resist was removed by blanket exposure to UV and washed with the developer. The wafer was subsequently rinsed with DIW and dried with nitrogen. The resulting structures are depicted in Fig. 3.3.

Access holes were etched using DRIE with the third lithography step from the backside of the wafer, Fig. 3.2(e). The back side was coated with photoresist AZ4620. The photoresist was spin coated at 300 rpm for 5 seconds, then 1800 rpm for 30 seconds, and finally 1600 rpm for 2 minutes. The resist was soft-baked at 90°C for 2 minutes. The exposed

photoresist was developed by a mixture with a volume ratio of 4:1 of AZ400K developer solution and DIW for 10 minutes. After rinsing in DIW and drying with N₂, the photoresist was hard-baked at 120°C for 15 minutes. The access holes were etched using DRIE for 4 hours. The front side of the wafer was protected by a dummy wafer bonded by a thin layer of AZ4620. After the etching step, the photoresist was removed in an acetone bath. The depth of the nanochannel can be further adjusted by growing a silicon oxide layer, Fig. 3.2(f). Finally, both nanochannels and microchannels were sealed by anodic bonding to a Pyrex glass wafer.

3.2.2 Results and Discussions

After completing the fabrication process, the nanochannels were observed under a microscope. A number of nanochannels were observed to be collapsing. To investigate the reason of the collapse and to optimize the aspect ratio of the nanochannels, nanochannels with various widths were fabricated, Fig. 3.4(a). The nanochannels were then filled with green fluorescence dye. Due to the weak fluorescent signal, a long exposure time up to one minute is needed to observe the nanochannels, Fig. 3.4(a,b). Since the nanochannels have a height smaller than the visible wavelength, a good channel can be identified as a bright field under a microscope. When a channel collapses, its image turns from white to grey and can be observed easily. For channels which are originally intact, the collapse can be initiated by pressing on the channel, Fig. 3.4(c). Once the top of the channel makes contact to its bottom, the collapse quickly spreads over the entire channel until completely covering it, except for the narrow region along the edge, Fig. 3.4(d). The results showed that nanochannels made in glass/silicon require a minimum aspect ratio (height to width) of about 4×10^{-3} , which is consistent with the results previously reported by Mao and Han [97].

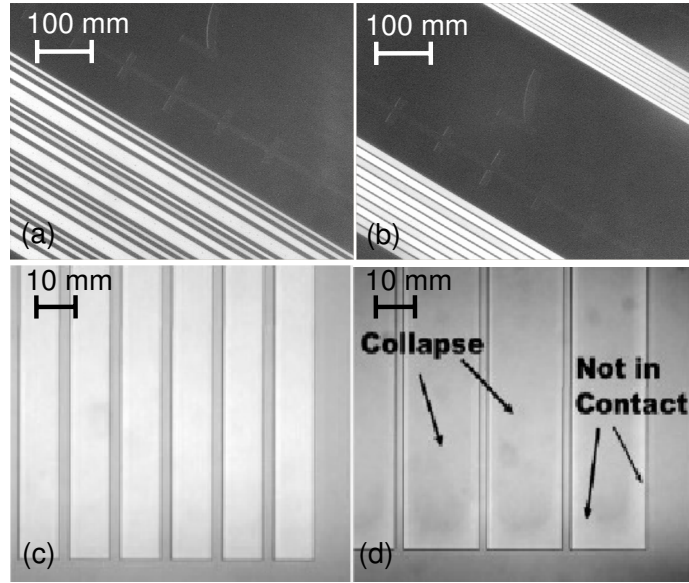


Figure 3.4: Nanochannel after bonding: (a) Filled nanochannels with different widths; (b) Filled nanochannels with the same width; (c) Good closed-end nanochannels with 10 μm width; (d) Collapsed nanochannels with 20 μm .

3.3 Fabrication of Polymeric Nanochannels

3.3.1 Materials and Methods

Materials

Thermoplastic materials allow remelting, remolding, and a higher flowability at the temperature higher than glass transition temperature T_g . Thus, thermoplastic polymers are ideal for fabricating nanochannels by thermal processes, such as hot embossing and thermal bonding. To make the observation, measurement, and analysis easier, a relatively high optical transparency is required. Besides, to enhance the durability of the final product, materials with better mechanical properties are desired. With the advantage of high optical transparency, toughness and hardness, good chemical resistance, as well as low cost and wide availability, poly(methyl methacrylate) (PMMA) is considered as a promising candidate for the fabrication of nanochannels. Sharing many common properties with PMMA but with better optical and mechanical properties but also more expensive, polycarbonate (PC) is also a considerable material for nanochannel fabrication. Important properties of PMMA are listed in Tab. 3.1, the data are from the supplier (GoodFellow Ltd.). PMMA (Poly(methyl methacrylate), Goodfellow Ltd., England) and PC (Polycarbonate, Goodfel-

Table 3.1: Mechanical, physical, and thermal properties of PMMA and PC.

Properties	Materials		Units
	PMMA	PC	
Mechanical properties			
Elongation at break	2.5-4	100-150	%
Hardness - Rockwell	M92-100	M70	
Izod impact strength	16-32	600-850	J m ⁻¹
Poisson ratio	0.35-0.4	0.37	
Tensile modulus	2.4-3.3	2.3-2.4	GPa
Tensile strength	80	55-75	MPa
Physical properties			
Abbe number	57.2	34.0	
Density	1.19	1.20	g cm ⁻³
Flammability	HB	V0-V2	
Refractive index	1.49	1.58	
Thermal properties			
Coefficient of thermal expansion	70-77	66-70	10 ⁻⁶ K ⁻¹
Heat-deflection temperature @ 0.45MPa	105	140	°C
Heat-deflection temperature @ 1.8MPa	95	128-138	°C
Glass transition temperature	105	155	°C
Specific heat	1400 - 1500	1200	J K ⁻¹ kg ⁻¹
Thermal conductivity @23C	0.17-0.19	0.19-0.22	W m ⁻¹ K ⁻¹

low Ltd., England) film with the polymeric thickness of 250 μm were used to fabricate the nanostructure reported in this thesis.

The negative images of the planar nanochannels were created on the surface of the silicon mold by employing standard photolithography and RIE process. The fabrication of the mold follows the same procedure as of the silicon-based nanochannel described in Section 3.2. Access reservoirs are created on the polymer by laser machining. The designs of the nanochannels on the silicon mold were transferred to the polymer surface by hot embossing, thus creating open nanochannels. Another piece of polymer was used to thermally bond to the embossed piece to create closed nanochannels with access reservoir. The channels and the reservoirs can also be fabricated on two different pieces before bonding. Figure 3.5 shows the overall fabrication process of the nanochannels. Temperature and pressure were recorded during the hot embossing and thermal bonding processes. Following, the detailed fabrication steps are described.

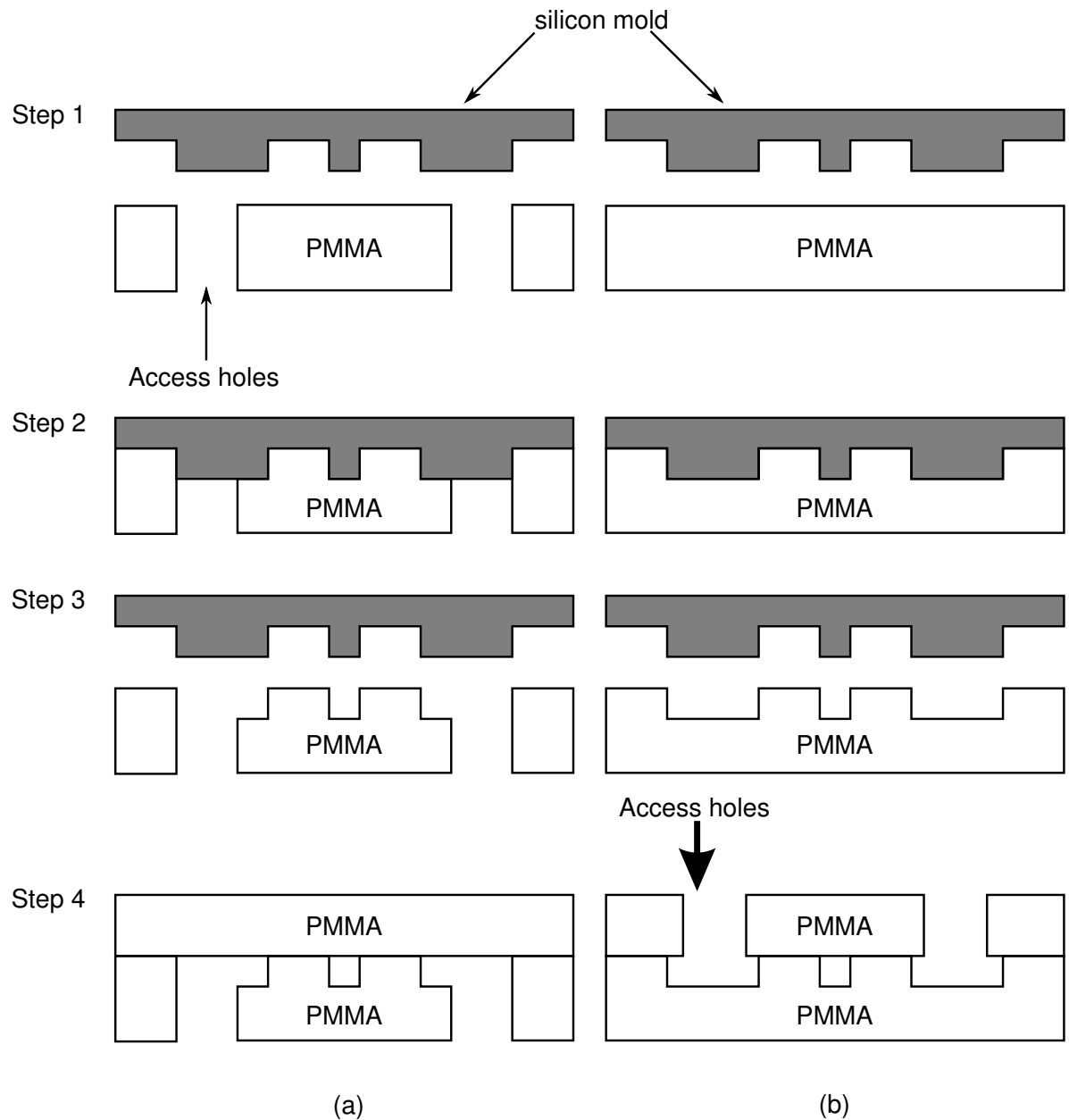


Figure 3.5: Fabrication process of nanochannels on a PMMA film. The channels and the access reservoirs can be created on the same piece (a) or on different pieces (b). Step 1: mold and material preparation; step 2: hot embossing; step 3: remove material from the mold; step 4: thermal bonding.

Mold Fabrication

The silicon mold was fabricated utilizing a four-inch silicon wafer with a thickness of 525 μm . The wafer was washed in piranha etch ($\text{H}_2\text{SO}_4 : \text{H}_2\text{O}_2$ with 3:1 volume ratio) for 10 minutes then rinsed with DIW and dried with nitrogen. The wafer was then dipped in buffered oxide etch for 1 minute then rinsed with DIW and dried with nitrogen. Subsequently, the wafer was baked at 120°C for 30 minutes. Next, a layer of hexamethyldisilazane was spin-coated on the wafer surface at the speed of 3000 rpm, acceleration of 3000 rpm/s for 30 seconds. The wafer was then spin-coated with photoresist (AZ1512, Clariant, Singapore) at the speed of 3000 rpm, acceleration of 3000 rpm/s for 30 seconds then baked at 100°C for 90 seconds. After an exposure with $20 \text{ mW}/\text{cm}^2$ UV light for 3 seconds using a contact aligner (MA6, Süss Microtec AG, Germany), the wafer is dipped in the developer (AZ developer, Clariant, Singapore) for 150 seconds then rinsed with DIW and dried with nitrogen. Etching was then performed with RIE (RIE-10NR, SAMCO Inc., Japan) with a RF power of 300 W, base pressure of 40 Pa, CF_4 flow rate of 30 sccm, and O_2 flow rate of 5 sccm. The photoresist layer was then removed by dipping the wafer in acetone for 10 minutes. The contact profiler (DEKTAK 6M, Veeco Instruments Inc., USA) was used to measure the etching rate. The result showed an etching rate of 1.26 nm/s, which is slow enough to control the depth of the nanopattern. The wafer was then diced in to pieces with the suitable size for the nanoimprinter (Eitre 3, Obducat, Sweden) to create the mold. The mold was then cleaned with oxygen plasma and spin-coated with a solution of 0.005% (Teflon AF 2400, DuPont, USA) in (FC-75, 3M, Canada). This layer prevents the material to stick on the mold surface after the hot embossing process. The thickness of this Teflon layer is estimated to be less than 5 nm. Spin-coating of the Teflon layer needs to be performed after two or three times of hot embossing.

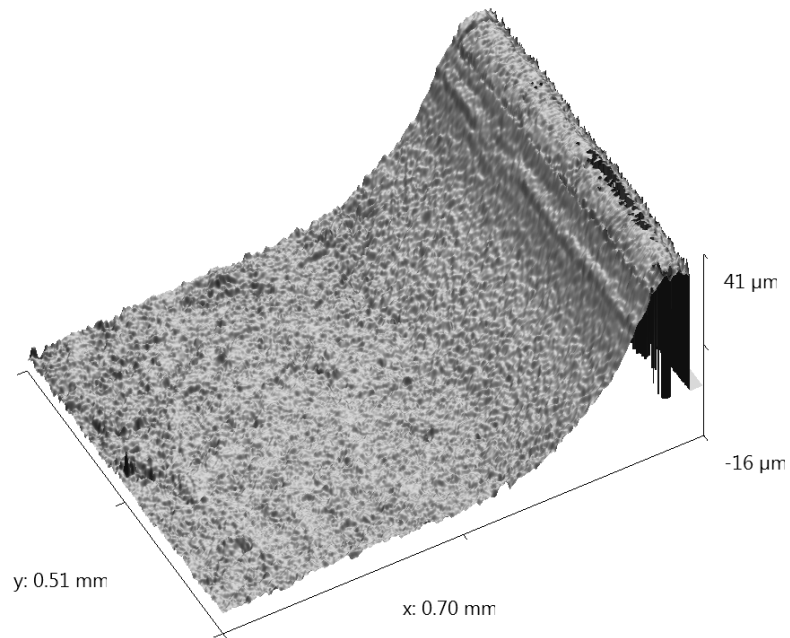
Laser Cutting

Prior to the hot embossing process, access reservoirs were machined on the polymer film by a laser cutter (M300-laser platform, Universal Laser Systems Inc., USA). Laser machining is a relatively accurate, inexpensive and rapid process, which is suitable for creating access reservoirs on the polymer film. One challenge in using laser machining is that

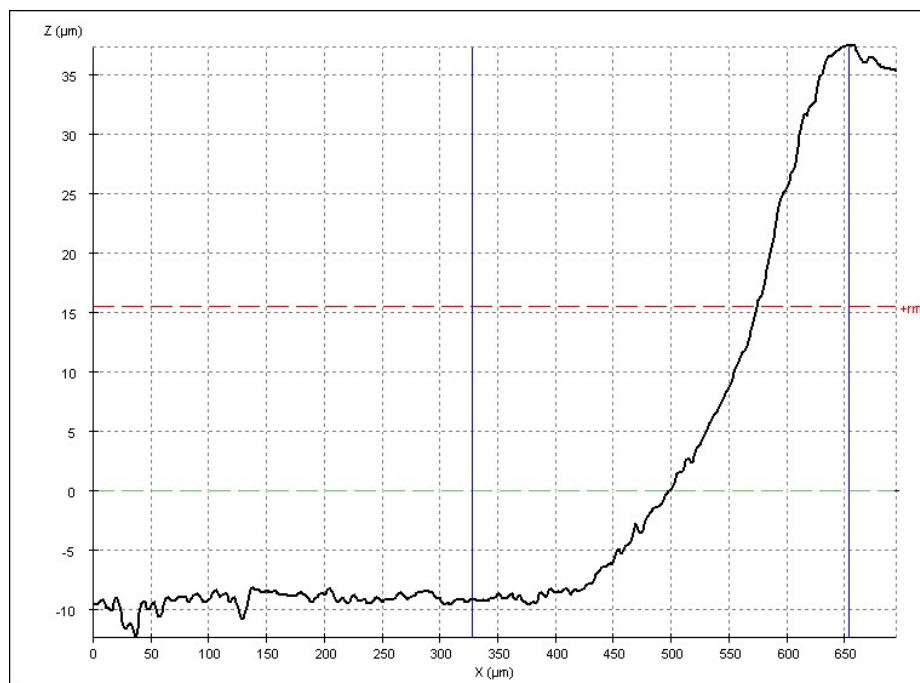
this process leaves ridges at the cutting line. The ridges are formed by the polymer residues during the ablation process. The height of these ridges can measure up to several tens of micrometers. Figure 3.6 shows a typical image of a ridge, with cross-sectional profile, captured by a confocal imaging profiler (PL μ , Sensofar, Spain). These ridges prevent full contact between the two pieces of polymer during the thermal bonding process and cause delamination. This problem reduces the durability of the final product. The geometry of the ridges can be controlled by choosing appropriate cutting parameters, such as cutting speed and laser power. Due to the complicated properties of the polymeric materials, as well as the environment parameters, optimal settings for the cutting process should be determined on a trial and error basis. Figure 3.7 shows the measured heights of the ridges at different speeds and laser powers. The results in Fig. 3.7 show that the ridge height decreases with increasing cutting speed and decreasing cutting power. However, sufficient power and cutting speed are needed for cutting through the polymer. The results also indicate that the ridges directly exposed to the laser are considerably higher than those at the opposite side.

Hot Embossing

Hot embossing was performed to transfer the nanopattern from the silicon mold to the polymer surface. A nanoimprint system (Eitre 3, Obducat, Sweden) was used for embossing. In this system, the force was applied by pressurized air while temperature was controlled through heating resistor in the supporting platform. The temperature was kept above glass transition temperature T_g of the material. Figure 3.8 explains the hot embossing process in details. An aluminium foil was used to distribute the pressure evenly. After the hot embossing process, the patterns on the PMMA film were investigated by an Atomic Force Microscope (AFM) to check the geometrical properties and to compare them with their counterparts on the silicon mold. The results show a good match between silicon mold and nanochannel on the polymer surface. Open channels with a depth down to 30 nm can be fabricated with high accuracy. Figure 3.9 shows a typical cross-section of a 30 nm depth open channel measured by AFM, in comparison to the corresponding pattern on the silicon mold. A typical hot embossing process at 150°C embossing temperature and 20 to 25 bar pressure takes about 15 minutes to complete. We observed that the visibility of the open nanochannels strongly depends on the process pressure and the process temperature.



(a)



(b)

Figure 3.6: A typical image of ridge created by laser cutting: (a) 3D image; (b) cross-sectional profile.

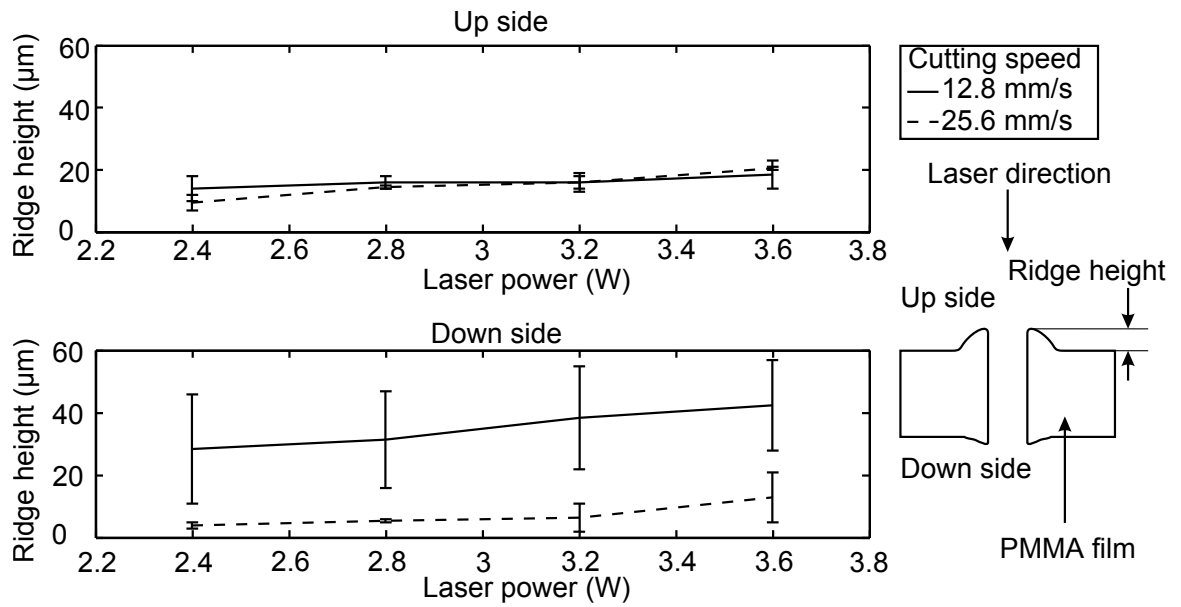


Figure 3.7: Ridge height measured for different laser cutting settings.

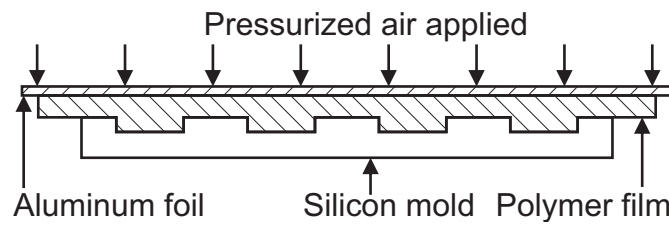


Figure 3.8: Hot embossing using PMMA film and silicon mold.

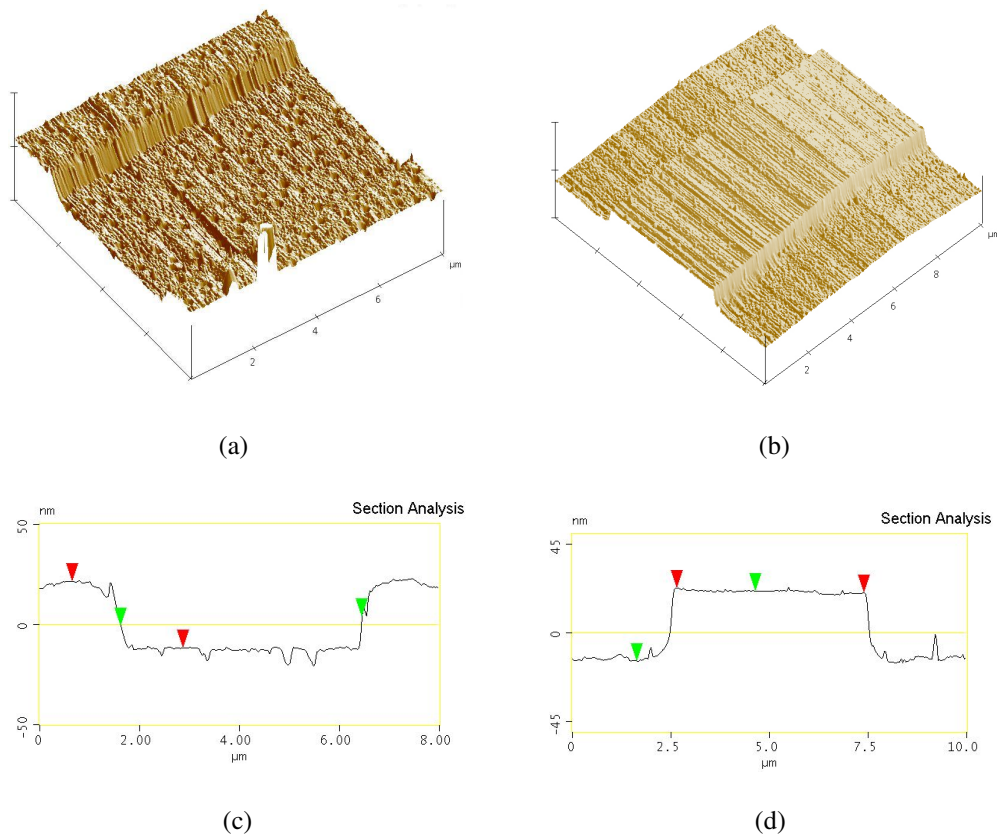


Figure 3.9: AFM images of nanochannels created by the hot embossing process: (a) 3D image of a channel created; (b) 3D image of a corresponding pattern on silicon; (c) Cross-sectional analysis, channel width $4.8\ \mu\text{m}$, channel depth $32.2\ \text{nm}$; (d) Cross-sectional analysis of a corresponding pattern on silicon wafer, width $4.7\ \mu\text{m}$, height $35.4\ \text{nm}$.

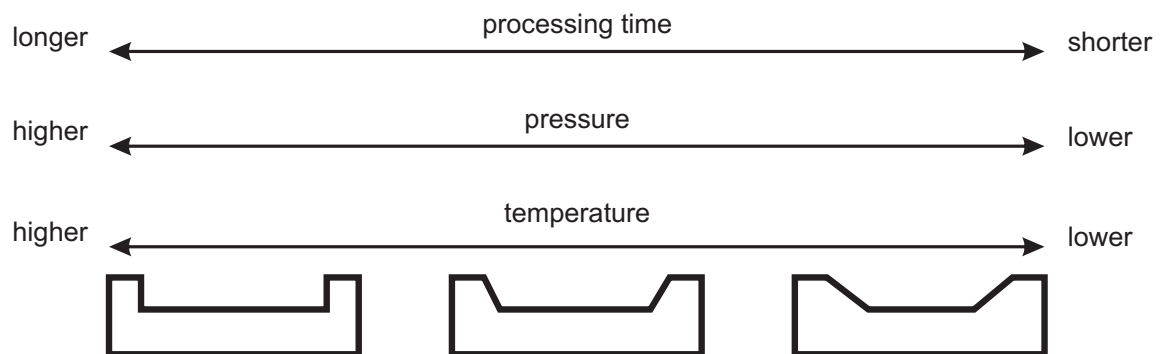


Figure 3.10: Cross section of a channel with different processing time, pressure, and temperature. Steeper slopes scatter more light and make the channels more visible.

Higher pressures and temperatures and longer processing time tend to produce more visible nanochannels, although the depths of those channels are almost the same. The difference in visibility can be explained by the slope steepness of the channel wall, Fig. 3.10. Steeper slopes tend to scatter more light, and therefore, make the channels more visible. Higher visibility of channels makes it easy for alignment and investigation of the channels in the subsequent process. However, excessive temperature and the pressure may damage the PMMA film. Degradation PMMA was observed at embossing temperature of 180°C and pressure above 20 bar. Therefore, relatively long processing time is desired to improve the visibility. Figures 3.11, 3.12, and 3.13 present AFM images of nanochannels with different processing time. The images show that for the processing time longer than 5 minutes, increasing the time does not affect the channel height.

Hot embossing was also carried out with PC (Polycarbonate, Goodfellow Ltd., England) film. Similar results as with PMMA film were achieved. However, many defects were found on the PC film surface after hot embossing. It is essential to know the cause of these defects and to eliminate them before PC can be used to fabricate the closed nanochannels. Images of the nanochannels fabricated using PC film, together with the embossing temperature and pressure are presented in Appendix A.

Thermal Bonding

To make closed PMMA nanochannels connected to micron/millimeter scale reservoirs, another piece of PMMA film was bonded on top of the fabricated nanochannels. Figure 3.14 shows two pieces of the chip to be bonded. Before bonding, the surfaces of both pieces were exposed to oxygen plasma to enhance adhesion. A plasma cleaner (Plasma Cleaner PDC-32G, Harrick Plasma, USA) was used. RF coil power was set to a “high” level (18 W) for 120 seconds. Air flow rate was regulated by the gas flow mixer (PlasmaFlo PDC-FMG-1, Harrick Plasma, USA) to maintain the chamber pressure of 300 Torr. It was observed that the treatment of the polymer surface with oxygen plasma can enhance the adhesion. Samples with lower plasma power (10.5 W) or shorter plasma treatment process time (60 second) showed poorer bonding behaviours. The standard thermal bonding process with a process temperature higher than the glass transition temperature T_g cannot be used, as the channels tend to collapse under the applied pressure when the temperature

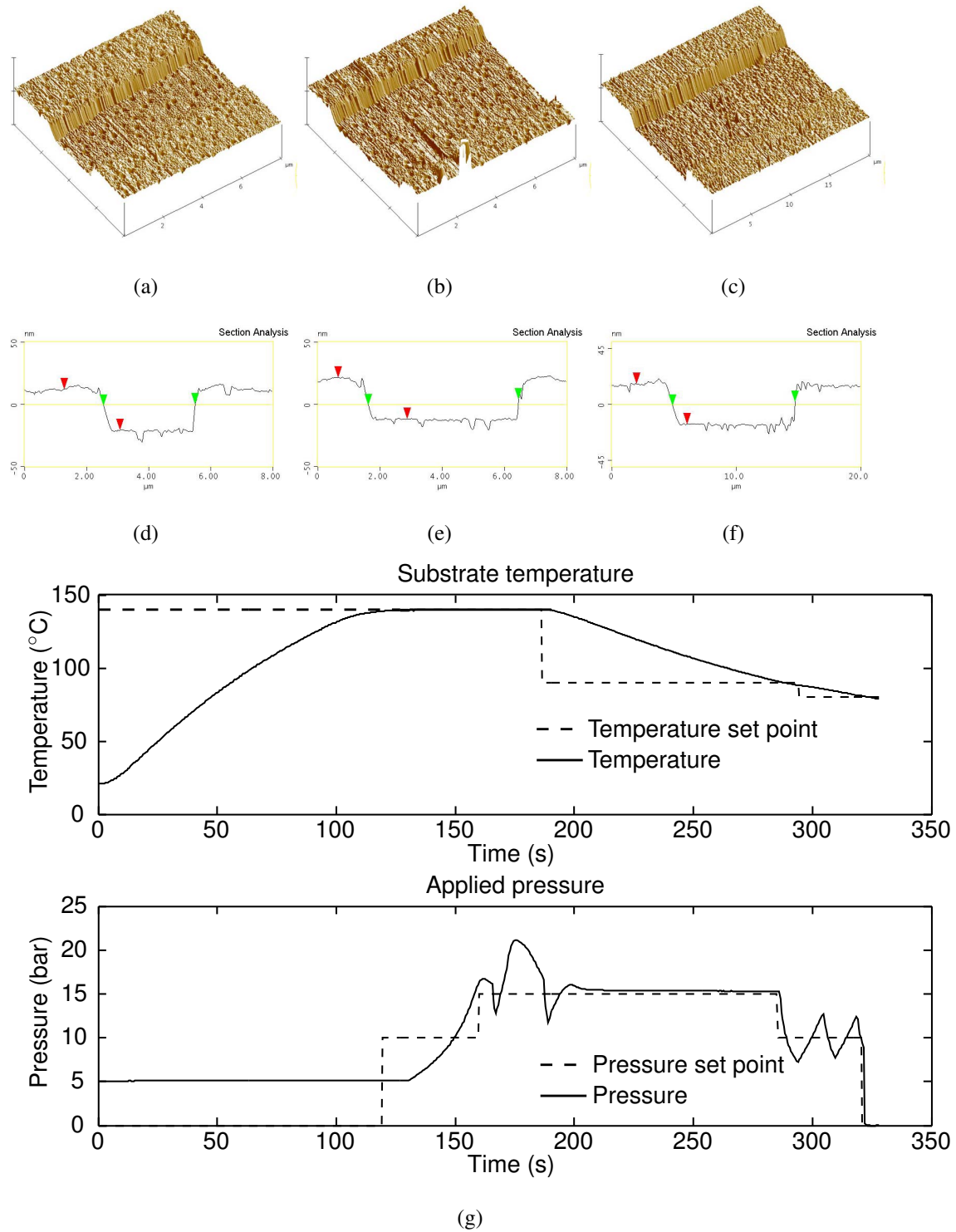


Figure 3.11: Image of channels with 5 minutes processing time: (a) 3D image of a small channel; (b) 3D image of a medium channel; (c) 3D image of a large channel; (d) cross-sectional image of a small channel shows a width of 2.97 μm , a height of 32.6 nm; (e) cross-sectional image of a medium channel shows a width of 4.81 μm , a height of 33.2 nm; (f) cross-sectional image of a large channel shows a width of 9.81 μm , a height of 32.7 nm; (g) temperature and pressure recorded during the hot embossing process.

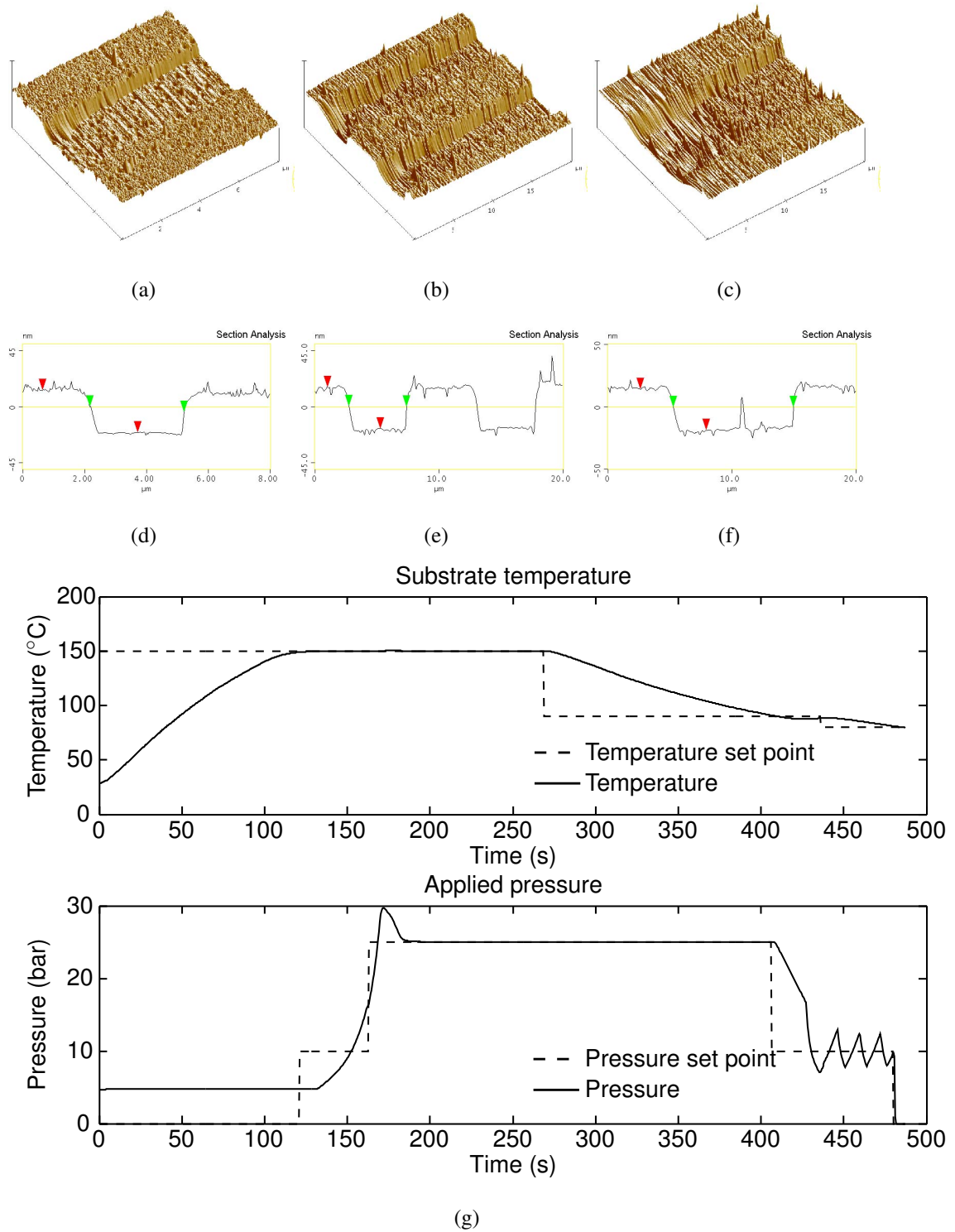


Figure 3.12: Image of channels with 7 minutes processing time: (a) 3D image of a small channel; (b) 3D image of a medium channel; (c) 3D image of a large channel; (d) cross-sectional image of a small channel shows a width of 3.06 μm , a height of 33.9 nm; (e) cross-sectional image of a medium channel shows a width of 4.70 μm , a height of 33.9 nm; (f) cross-sectional image of a large channel shows a width of 9.69 μm , a height of 32.9 nm; (g) temperature and pressure recorded during the hot embossing process.

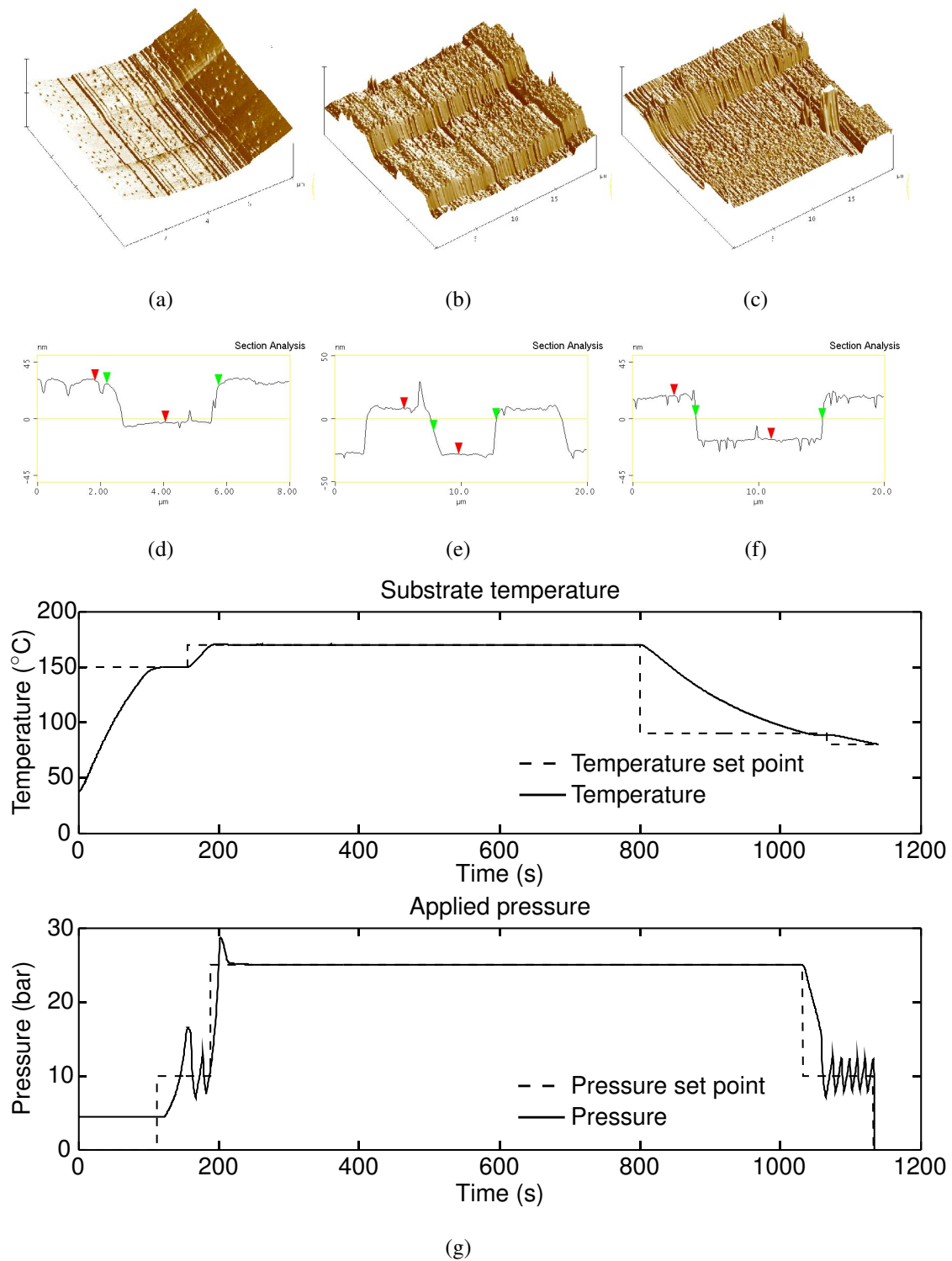


Figure 3.13: Image of channels with 20 minutes processing time: (a) 3D image of a small channel; (b) 3D image of a medium channel; (c) 3D image of a large channel; (d) cross-sectional image of a small channel shows a width of 2.94 μm , a height of 34.8 nm; (e) cross-sectional image of a medium channel shows a width of 4.92 μm , a height of 37.9 nm; (f) cross-sectional image of a large channel shows a width of 10.1 μm , a height of 35.1 nm; (g) temperature and pressure recorded during the hot embossing process.

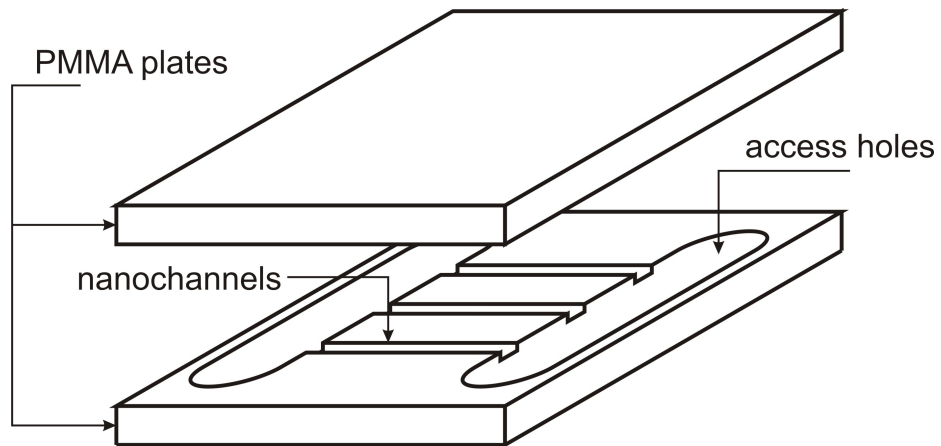


Figure 3.14: PMMA cap is bonded to make close channels.

approaches T_g . The channels started to collapse at a temperature of 95°C, a pressure of 15 bar and a process time of 30 minutes. Therefore, low-temperature thermal bonding was used. Thermal bonding was also performed with the nanoimprinter (Eitre 3, Obducat, Sweden). However, a lower temperature below T_g , a lower pressure, and a longer process time were applied. A typical thermal bonding process takes less than 30 minutes, depending on the cooling process of the substrate, the bonding temperature was set at 85°C and the pressure is set at 10 bar. Bonding cannot be achieved with temperature of 80°C or below. Logged temperature and pressure of a thermal bonding process is shown in Fig. 3.15.

3.3.2 Results and Discussions

Figure 3.16 shows a set of closed channels after thermal bonding. The channel height in this specimen is 300 nm. Lower channel height requires a narrower range of thermal bonding temperature as well as pressure. Capillary filling experiments were carried out with the fabricated channels using 99% isopropanol. It was found that liquid can penetrate into the nanochannel. However, a higher percentage of blocked channels still exists. The process must be fine tuned to increase the yield. Similar nanochannels created on a 1-mm PMMA plate give more consistent experimental results and was used in our capillary filling experiment. Detailed of filling experiments in PMMA nanochannels are described in Chapter 4.

In conclusion, first attempts have shown the possibility of fabricating nanochannel on

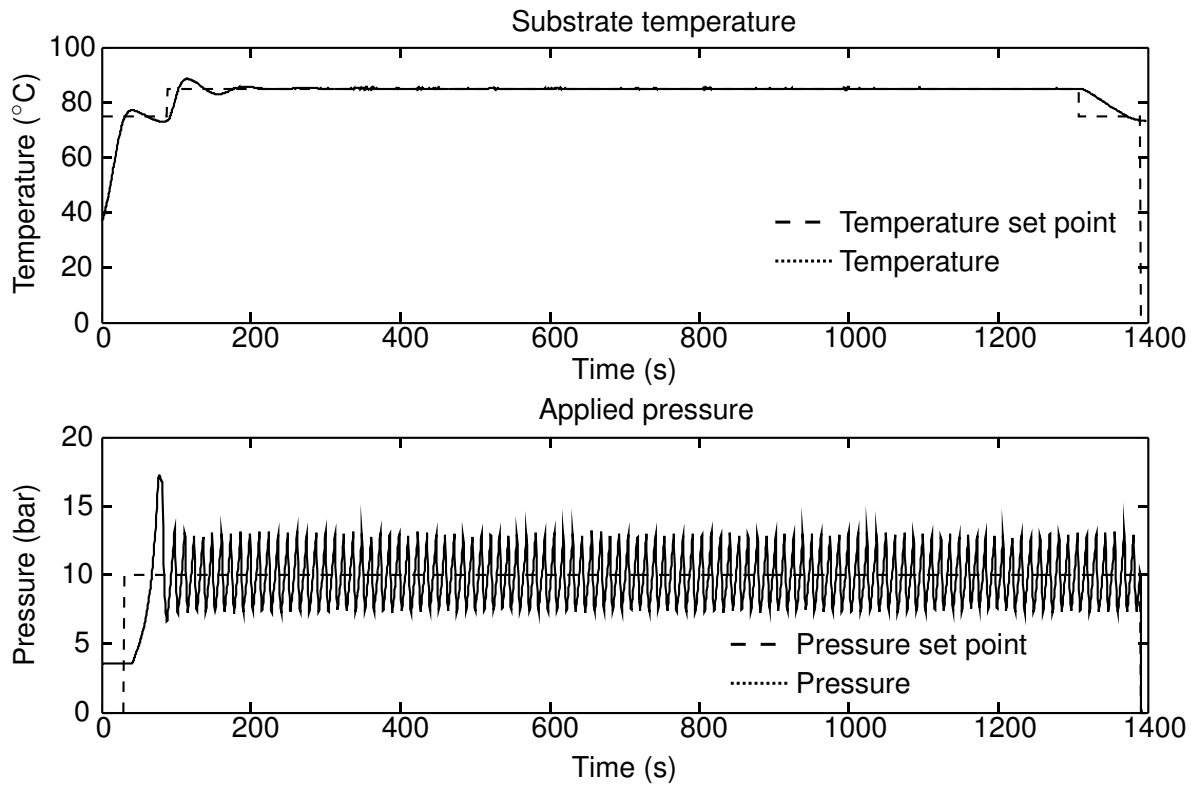


Figure 3.15: Temperature and pressure recorded during a typical thermal bonding process.

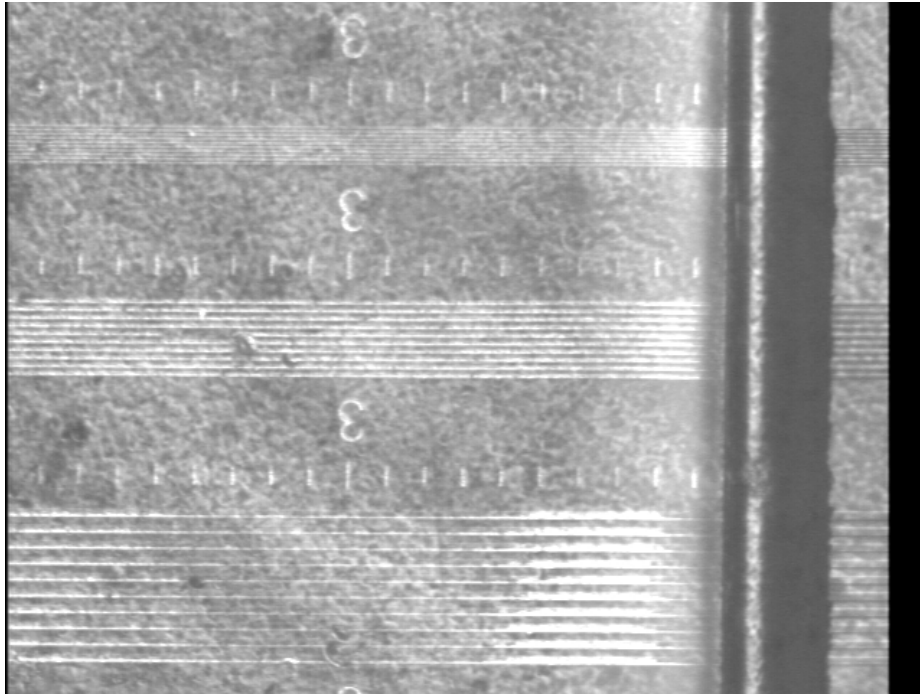


Figure 3.16: A set of nanochannel created after thermal bonding process. Region on the left is the access reservoir. The widths of nanochannels in the top, middle, and below groups are 1 μm , 5 μm , and 3 μm respectively.

polymer film using hot embossing and thermal bonding. Open channels with depth down to 30 nm and close channels of 300 nm height were fabricated. Some challenges in fabrication were identified, including avoiding the formation of ridge during reservoir fabrication, reducing adhesion between material and mold during hot embossing process, avoiding channel collapse during thermal bonding, and the control of temperature and pressure during thermal bonding to achieve good adhesion.

Chapter 4

Filling in Open-End Nanochannels

4.1 Background

Mass transport in nanoscale involves multiple physics. Many of them did not have a completed theoretical description. Many investigations were done in the field, however, not all of them gave consistent results. Nanochannels provide a deterministic platform to study the mass transport phenomena in nanoscale. Capillary filling in open-end nanochannels is a relatively simple experiment, yet it is effective in exploring the surface force and the fluid flow in nanochannels. Capillary filling occurs spontaneously in nanochannels. The filling speed is usually adequate to record with a standard image recorder and a suitable microscope. The capillary filling in planar nanochannels is most visible under a microscope and also most suitable to be idealized by a one-dimension model.

The capillary filling process is traditionally described by Washburn's theory [33]. The theory predicts a linear relationship between the filling time and square of the filling length. This theory is proven to be accurate down to microscale. For example, recent study by Hultmark et. al. [98] on the effect of gas displacing in capillary filling in microchannels showed that even though the inertia of gas in the channels can slow down the filling process at the first stage, the filling quickly approach the classical prediction given by Washburn.

Several works have been done on capillary filling in nanochannels. Most experimental results showed discrepancies from the classical Washburn's theory, which is still valid at microscale. Many experiments showed a lower filling compared to the classical theory.

This phenomenon is usually accounted as the direct result of the electroviscous effect, because such effect is verified in pressure-driven or electroosmosis-driven flow. Due to the same reason, the electroviscous effect in capillary filling is usually described by the theories borrowed from pressure-driven or electroosmosis-driven flow [99], despite the principle differences between those phenomena.

Electroviscous effect is the increase in apparent viscosity caused by electric force acting on the electric double layer (EDL) formed at the interface between a fluid and a solid. Details on the formation of the EDL is presented in the next section. The thickness of the EDL is represented by the Debye length, which is typically in nanoscale. In microchannels or larger channels, the EDL is too small in comparison to the channel size. Therefore, the electroviscous effect is negligible. However, in nanochannels, the contribution of this effect in transport phenomena such as pressure driven flow or capillary filling need to be investigated, especially in the case of capillary filling, where the observed discrepancies between the experimental results and the classical theory are significant and complicated. Such a theoretical evaluation also helps to predict if there are other phenomena involved in the capillary filling process.

In this chapter, we establish a theoretical model on the electroviscous effect, particularly for capillary filling. The result from this model is then compared to experimental data to judge how much the electroviscous effect contributes to the discrepancy of capillary filling speed in nanochannels.

4.2 Theoretical Analysis

4.2.1 Problem Description

Figure 4.1 describes the geometry for the model of capillary filling in a nanochannel with a height of h and a width of w . The channel is of high aspect ratio $w/h \gg 1$ and can be considered as a slit between two parallel plates. The channel wall is positively charged. The shaded areas in Fig. 4.1 represent the EDL, containing the compact layer attached to the channel wall and the mobile layer. When a liquid flows along the nanochannel, the absorption of positive charge into the wall causes negative ions to accumulate at the meniscus.

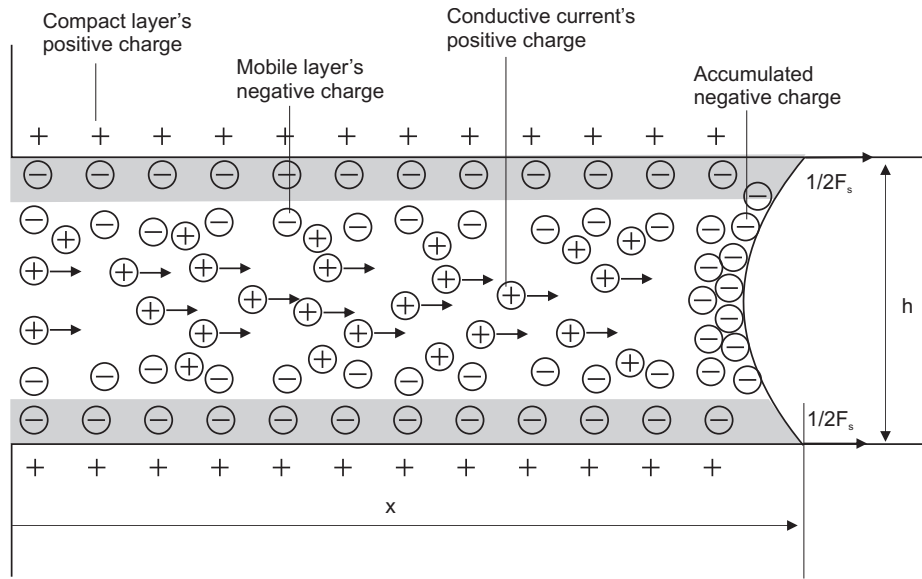


Figure 4.1: Capillary filling in a nanochannel: Ions distribution and movement inside a liquid column moving in a nanochannel due to capillary filling.

Charge imbalance between the meniscus and the channel inlet induces a streaming voltage. This streaming voltage generates a conductive current.

4.2.2 Governing Equations and Assumptions

The capillary filling phenomenon in a nanochannel is assumed to be governed by following physics and assumptions:

- **Continuum assumption:** The Knudsen number Kn represents the ratio of the molecular mean-free path to the characteristic length. In order to apply continuum assumption, low Knudsen number is required [100]. For most of liquids, the mean-free path is in the order of few nanometers. Thus, even in nanochannels with a height from tens to several hundreds nanometers, the continuum assumption ($Kn < 10^{-1}$) is still valid.
- **Surface tension:** Surface tension is the key driving force for capillary filling phenomenon. The driving force depends on the surface tension of the fluid and the contact angle between the fluid and the channel wall.
- **Pressure driven flow:** Due to the surface tension at the front surface, the static pres-

sure drops across the meniscus. Therefore, fluid flow inside the channel is caused by the pressure difference between the channel entrance and at the meniscus just inside the fluid. In this model, the pressure driven phenomenon is assumed to dominate, so the velocity profile is assumed to have the same form as that in pressure driven flow.

- **Charge balance:** When the fluid moves inside the nanochannel, due to absorption and defect on material surface, ions in the fluid attach to the channel walls. To satisfy the electric charge conservation, we assume that there is a region near the front surface where electric charge density is different from those at the rest of fluid body. The total electric charge in this region (called accumulated charge q_a) creates an electric field, which in turn drives the conductive current. The charge balance is considered for the total charge of the fluid body, total charge on the channel wall, the accumulated charge, the streaming current and the conductive current.
- **Charge density distribution:** Ion absorption at the channel wall creates an electric field across the channel height, leading to the redistribution of charge density inside the channel. The charge density distribution is governed by the Poisson-Boltzmann (PB) equation. At low zeta potential, Debye-Hückel approximation can be applied to linearise the PB equation.
- **Electrostatic interaction:** Electrostatic interaction between the accumulated charge and the total charge of the whole fluid body slows down the capillary filling process. This model assumes that the electric field created by the accumulated charge is concentrated only in the nanochannel. This assumption makes sense if the permittivity of the fluid is much higher than those of air and of the channel material. Electrostatic interaction is governed by Gauss's theorem and Lorentz's force law.
- **Viscous force:** Viscous force is significant in the nanoscale. In our model, viscous force is calculated using one dimensional laminar flow between two infinite parallel plates. The velocity profile is assumed to be parabolic.
- **Newton's second law:** Finally, the effect of all forces on the dynamics of the fluid column is calculated by Newton's second law, which states that derivative of mo-

mentum of an object with respect to time is equal to the total force acting on that object.

4.2.3 Surface Tension and Capillary Filling

The pressure difference across the meniscus of a moving liquid column is given by the Young-Laplace equation:

$$\Delta P = \sigma \left(\frac{1}{r_1} + \frac{1}{r_2} \right) \quad (4.1)$$

where ΔP is the pressure difference, σ is the surface tension, r_1 and r_2 are the principle radii of curvature.

Figure 4.1 shows the forces acting on the meniscus. Assuming $w \gg h$, the surface force F_s caused by surface tension is:

$$F_s = 2\sigma w \cos \theta \quad (4.2)$$

where θ is the contact angle between the fluid and the wall surface, w is the channel width, h is the channel height. The capillary filling flow can be considered as a pressure-driven flow, except the fact that at the front surface region, the velocity profile of capillary filling has a plug-like shape.

In this model, we are interested in cases where the electric force is relatively small compared to the surface force, so that the velocity profile of the fluid flow is approximately similar to that in pressure driven flow. The velocity profile of an one-dimensional laminar pressure driven flow between two infinite parallel plates is given by [101]:

$$u = -\bar{u} \left(6\frac{y^2}{h^2} - \frac{3}{2} \right), \quad -\frac{h}{2} < y < \frac{h}{2} \quad (4.3)$$

where u is the fluid velocity, $\bar{u}$ is the average velocity across the channel height, y is the coordinate across the channel height. The origin of coordinate is on the center plane.

The average velocity $\bar{u}$ is assumed to be equal to the meniscus velocity. In this thesis, the symbol $\bar{u}$ represents both the meniscus velocity and the average velocity across the the channel height. With the above assumptions, the viscous force acting on the whole fluid body is

$$F_v = \left(\mu \frac{d}{dy} u \Big|_{y=\frac{h}{2}} - \mu \frac{d}{dy} u \Big|_{y=-\frac{h}{2}} \right) wx = -\frac{12\mu\bar{u}}{h} wx \quad (4.4)$$

where F_v is the viscous force act on the fluid and μ is the dynamic viscosity of the fluid.

4.2.4 Charge Density Distribution

One of the key elements involved in the electric force acting on the fluid is the charge density distribution. In a nanochannel, the potential distribution, and hence, charge density distribution, is governed by the PB equation:

$$\nabla^2 \psi = -\frac{\rho_q}{\epsilon \epsilon_0} = -\frac{e}{\epsilon \epsilon_0} \sum_i z_i n_i^0 \exp\left(-\frac{z_i e \psi}{kT}\right) \quad (4.5)$$

where ψ is the electrostatic potential, ρ_q is the charge density, z_i is the charge number of ionic species i , n_i^0 is the concentration of ionic species i , and other symbols as defined in Eq. (2.1)

For a symmetric binary electrolyte ($z_+ = -z_- = z$), Eq. (4.5) can be written as:

$$\nabla^2 \tilde{\psi} = \frac{\kappa^2}{z} \sinh(z \tilde{\psi}) \quad (4.6)$$

where $\tilde{\psi} = \frac{e\psi}{kT}$ and κ is the inverse of the Debye length:

$$\kappa^2 = \frac{2e^2 z^2 n_0}{\epsilon \epsilon_0 kT} \quad (4.7)$$

If the electrostatic potential is low (i.e., Debye-Hückel approximation $z \tilde{\psi} < 1$), Eq. (4.6) can be written as:

$$\nabla^2 \tilde{\psi} = \kappa^2 \tilde{\psi} . \quad (4.8)$$

Equation (4.8) is a linear equation whose solution can be obtained analytically. The condition $z \tilde{\psi} < 1$ is applied at room temperature ($T = 300$ K) and $z = 1$ as:

$$z \tilde{\psi} = \frac{ze\psi}{kT} < 1 , \quad (4.9)$$

as a result:

$$\psi \leq \zeta < \frac{kT}{e} \approx 26 \text{ mV} \quad (4.10)$$

where ζ (zeta potential) is the electric potential at the boundary between the compact layer and mobile layer. The zeta potential ζ is approximately the same as electric potential at the channel wall ψ_s .

In the model presented here, the Debye-Hückel approximation is assumed. Solution for PB equation for a slit-shaped channel under Debye-Hückel approximation is given by:

$$\psi(y) = \psi_s \frac{\cosh(-\kappa y)}{\cosh(\kappa h/2)} = \zeta \frac{\cosh(-\kappa y)}{\cosh(\kappa h/2)}, \quad -\frac{h}{2} \leq y \leq \frac{h}{2} . \quad (4.11)$$

So, the charge density distribution is:

$$\rho_q = -\epsilon\epsilon_0 \frac{d^2\psi}{dy^2} = -\epsilon\epsilon_0 \zeta \kappa^2 \frac{\cosh(\kappa y)}{\cosh(\frac{\kappa h}{2})}, \quad -\frac{h}{2} \leq y \leq \frac{h}{2}. \quad (4.12)$$

4.2.5 Conductivity of Electrolyte

The conductivity of electrolyte in a nanochannel must be calculated by considering the contribution of individual ionic species. The expression for conductivity of the electrolyte is:

$$\lambda = \sum_i \lambda_i = \sum_i |z_i| e v_i n_i \quad (4.13)$$

where λ is the total conductivity of the electrolyte, λ_i is the individual contribution of ionic species i to the conductivity, z_i is the charge number, v_i is the electric mobility of, and n_i is the concentration of the ionic species i .

Applying PB equation:

$$n_i = n_0 \exp(-z_i \tilde{\psi}) \quad (4.14)$$

and substituting (4.14) into (4.13) give:

$$\lambda = \sum_i \lambda_i = n_0 \sum_i |z_i| e v_i \exp(-z_i \tilde{\psi}) \quad (4.15)$$

which leads to the average conductivity across the channel height:

$$\bar{\lambda} = \frac{1}{h} \int_{-\frac{h}{2}}^{\frac{h}{2}} \lambda dy = n_0 \frac{1}{h} e \int_{-\frac{h}{2}}^{\frac{h}{2}} \sum_i |z_i| v_i \exp(-z_i \tilde{\psi}) dy. \quad (4.16)$$

With the Debye-Hückel approximation, Eq. (4.16) can be expressed as:

$$\bar{\lambda} = n_0 \frac{1}{h} e \int_{-\frac{h}{2}}^{\frac{h}{2}} \sum_i |z_i| v_i (1 - z_i \tilde{\psi}) dy. \quad (4.17)$$

If a monovalent electrolyte such as the NaCl solution ($z_+ = -z_- = 1$) is considered, Eq. (4.17) can be rewritten as:

$$\bar{\lambda} = n_0 e (v_+ + v_-) \left(1 + \frac{1}{h} \frac{v_- - v_+}{v_+ + v_-} \int_{-\frac{h}{2}}^{\frac{h}{2}} \tilde{\psi} dy \right). \quad (4.18)$$

Substituting the solution of the potential distribution (4.12) into (4.18) and performing the integration result in:

$$\bar{\lambda} = n_0 e (v_+ + v_-) \left[1 + \frac{\zeta e}{kT} \frac{v_- - v_+}{v_+ + v_-} \frac{2 \tanh(\frac{\kappa h}{2})}{\kappa h} \right]. \quad (4.19)$$

Defining the molar conductivity of a monovalent electrolyte as $\Lambda_m = \sum_i e N_A v_i$, we obtain the expression for the average conductivity as:

$$\bar{\lambda} = n_0 \frac{\Lambda_m}{N_A} \left[1 + \frac{\zeta e}{kT} \frac{v_- - v_+}{v_+ + v_-} \frac{2 \tanh\left(\frac{\kappa h}{2}\right)}{\kappa h} \right]. \quad (4.20)$$

For NaCl, the electric mobilities of Na^+ and Cl^- are $51.9 \times 10^{-9} \text{ Vsm}^{-2}$ and $79.1 \times 10^{-9} \text{ Vsm}^{-2}$ respectively [102]. However, these values are only accurate for a highly diluted concentration. The mobilities are lower at higher concentrations. In this thesis, the above values are taken for further analysis.

4.2.6 Charge Balance

Let's call the accumulative charge at the meniscus q_a , the streaming current is:

$$I_s = \int_{\mathcal{A}} u \rho_q d\mathcal{A} = \int_{-\frac{h}{2}}^{\frac{h}{2}} u \rho_q w dy \quad (4.21)$$

and the conduction current is:

$$I_c = - \frac{U_s \bar{\lambda} \mathcal{A}}{x} \quad (4.22)$$

where U_s is the streaming potential and $\mathcal{A}$ is the cross-sectional area of the channel:

$$\mathcal{A} = wh. \quad (4.23)$$

Charge balance for the whole fluid body inside a channel requires that:

$$I_{\text{total}} = \frac{d}{dt} q_{\text{total}} \quad (4.24)$$

where q_{total} is the total charge in the control volume and I_{total} is the total current entering the control volume.

Let's call δ_b the longitudinal electric charge density of the fluid body along the channel and δ_w the longitudinal electric charge density of the channel wall, the steady state condition requires:

$$\delta_b = -\delta_w. \quad (4.25)$$

The above condition is assumed for the capillary filling model. Implementing the charge balance (4.24):

$$I_c + I_s = \frac{d}{dt} (\delta_b x + \delta_w x + q_a) \quad (4.26)$$

where $I_c + I_s$ is the total current entering the channel and q_a is the accumulated charge. Substituting (4.21), (4.22), (4.23), (4.25) into (4.26) leads to

$$-\frac{U_s \bar{\lambda} w h}{x} + \int_{-\frac{h}{2}}^{\frac{h}{2}} u \rho_q w dy = \frac{d}{dt} q_a . \quad (4.27)$$

4.2.7 Newton's Second Law

Applying Newton's second law to the whole fluid column leads to:

$$F_s + F_v + F_e = \frac{d}{dt} (\rho_m w h x \bar{u}) \quad (4.28)$$

where F_e is the electric force caused by the accumulated charge and ρ_m is the mass density of the fluid. The surface force F_s and the viscous force F_v are given by the Eqs. (4.2) and (4.4) respectively. The electric charge accumulating at the meniscus creates an electric field, which causes a force acting on the whole fluid column. In this model, the electric field is kept constant and parallel along the channel. The electric force reads:

$$F_e = -x \int_{\mathcal{A}} \frac{U_s}{x} \rho_q d\mathcal{A} = -w x \int_{-\frac{h}{2}}^{\frac{h}{2}} \frac{U_s}{x} \rho_q dy . \quad (4.29)$$

Applying Gauss's theorem around the meniscus region, where the accumulated charge locates, leads to:

$$-E_s = \frac{U_s}{x} = \frac{q_a}{A_c \epsilon \epsilon_0} = \frac{q_a}{w h \epsilon \epsilon_0} \quad (4.30)$$

where E_s is the streaming electric field strength. Substituting (4.30) into (4.29) results in:

$$F_e = -x \int_{\mathcal{A}} \frac{U_s}{x} \rho_q d\mathcal{A} = -x \int_{-\frac{h}{2}}^{\frac{h}{2}} \frac{q_a}{h \epsilon \epsilon_0} \rho_q dy = -\frac{q_a x}{h \epsilon \epsilon_0} \int_{-\frac{h}{2}}^{\frac{h}{2}} \rho_q dy . \quad (4.31)$$

Also, substituting (4.30) into (4.27) results in:

$$-\frac{q_a \bar{\lambda}}{\epsilon \epsilon_0} + \int_{-\frac{h}{2}}^{\frac{h}{2}} u \rho_q w dy = \frac{d}{dt} q_a . \quad (4.32)$$

Putting (4.3), (4.4), (4.28), (4.2), (4.31) and (4.32) together leads to the equation system:

$$\begin{cases} 2\sigma w \cos \theta - \frac{12\mu \bar{u}}{h} w x - \frac{q_a x}{h \epsilon \epsilon_0} \int_{-\frac{h}{2}}^{\frac{h}{2}} \rho_q dy & = \frac{d}{dt} (\rho_m w h x \bar{u}) \\ -\frac{q_a \bar{\lambda}}{\epsilon \epsilon_0} + \bar{u} w \int_{-\frac{h}{2}}^{\frac{h}{2}} \left(\frac{3}{2} - 6 \frac{y^2}{h^2} \right) \rho_q dy & = \frac{d}{dt} q_a . \end{cases} \quad (4.33a)$$

$$\begin{cases} 2\sigma w \cos \theta - \frac{12\mu \bar{u}}{h} w x - \frac{q_a x}{h \epsilon \epsilon_0} \int_{-\frac{h}{2}}^{\frac{h}{2}} \rho_q dy & = \frac{d}{dt} (\rho_m w h x \bar{u}) \\ -\frac{q_a \bar{\lambda}}{\epsilon \epsilon_0} + \bar{u} w \int_{-\frac{h}{2}}^{\frac{h}{2}} \left(\frac{3}{2} - 6 \frac{y^2}{h^2} \right) \rho_q dy & = \frac{d}{dt} q_a . \end{cases} \quad (4.33b)$$

Note that $\bar{u} = \dot{x}$. Two new variables are introduced to simplify the system above and to keep it as a first order system: $\hat{q}_a = \frac{q_a}{w}$, $\chi = x\bar{u} = x\dot{x}$. The system of equations (4.33) becomes:

$$\begin{cases} 2\sigma \cos \theta - \frac{12\mu}{h}\chi - \frac{\hat{q}_a x}{h\epsilon\epsilon_0} \int_{-\frac{h}{2}}^{\frac{h}{2}} \rho_q dy & = \rho_m h \dot{\chi} \\ -\frac{\hat{q}_a \bar{\lambda}}{\epsilon\epsilon_0} + \dot{x} \int_{-\frac{h}{2}}^{\frac{h}{2}} \left(\frac{3}{2} - 6\frac{y^2}{h^2} \right) \rho_q dy & = \dot{q}_a \\ \chi & = x\dot{x} . \end{cases} \quad \begin{matrix} (4.34a) \\ (4.34b) \\ (4.34c) \end{matrix}$$

Let's call $\hat{F}_s = \frac{F_s}{w} = 2\sigma \cos \theta$, $A = \frac{12\mu}{h}$, $B = \frac{1}{h\epsilon\epsilon_0} \int_{-\frac{h}{2}}^{\frac{h}{2}} \rho_q dy$, $C = \rho_m h$, $D = \frac{\bar{\lambda}}{\epsilon\epsilon_0}$, and $E = \int_{-\frac{h}{2}}^{\frac{h}{2}} \left(\frac{3}{2} - 6\frac{y^2}{h^2} \right) \rho_q dy$. Equation (4.12) is used to calculate the two parameters B and E :

$$\begin{aligned} B &= -\frac{\zeta \kappa^2}{h} \int_{-\frac{h}{2}}^{\frac{h}{2}} \frac{\cosh(\kappa y)}{\cosh(\frac{\kappa h}{2})} dy \\ &= -\frac{2\zeta \kappa}{h} \tanh \left[\frac{\kappa h}{2} \right] \end{aligned} \quad (4.35)$$

$$\begin{aligned} E &= -\epsilon\epsilon_0 \zeta \kappa^2 \int_{-\frac{h}{2}}^{\frac{h}{2}} \left(\frac{3}{2} - 6\frac{y^2}{h^2} \right) \frac{\cosh(\kappa y)}{\cosh(\frac{\kappa h}{2})} dy \\ &= -\frac{12\epsilon\epsilon_0 \zeta \left[\kappa h - 2 \tanh \left(\frac{\kappa h}{2} \right) \right]}{\kappa h^2} . \end{aligned} \quad (4.36)$$

The system of equations (4.34) becomes:

$$\begin{cases} \hat{F}_s - A\chi - B\hat{q}_a x & = C\dot{\chi} \\ -D\hat{q}_a + E\dot{x} & = \dot{q}_a \\ \chi & = x\dot{x} \end{cases} \quad \begin{matrix} (4.37a) \\ (4.37b) \\ (4.37c) \end{matrix}$$

with all parameters determined.

This set of first order ordinary differential equations (ODEs) is non-linear, so an analytical solution is difficult to obtain. Therefore, this equation system needs a numerical solution.

4.2.8 Numerical Solutions

Equations for displacement, velocity and accumulated charge are given by the system of equations (4.37). For capillary filling effect in nanochannels, it is suitable to apply the

initial conditions (ICs):

$$\left\{ \begin{array}{lcl} x(0) & = & 0 \end{array} \right. \quad (4.38a)$$

$$\left\{ \begin{array}{lcl} \chi(0) & = & 0 \end{array} \right. \quad (4.38b)$$

$$\left\{ \begin{array}{lcl} \hat{q}_a(0) & = & 0 . \end{array} \right. \quad (4.38c)$$

In many previous works, one IC is $\dot{x}(0) = 0$, because Newton's second law requires that a sudden increase in momentum is prohibited. In this model, that requirement is fulfilled by the IC $\chi(0) = 0$. Therefore, the IC $\dot{x}(0) = 0$ is not necessary.

In order to apply for the Runge-Kutta method, the equation system needs to be written in the form of:

$$\frac{d}{dt} \begin{bmatrix} \chi \\ \hat{q}_a \\ x \end{bmatrix} = f \begin{bmatrix} \chi \\ \hat{q}_a \\ x \end{bmatrix} \quad (4.39)$$

where f is any vector function.

System of equations (4.37) can be written according to (4.39) as:

$$\left\{ \begin{array}{lcl} \dot{\chi} & = & \frac{\hat{F}_s}{C} - \frac{A}{C}\chi - \frac{B}{C}\hat{q}_a x \end{array} \right. \quad (4.40a)$$

$$\left\{ \begin{array}{lcl} \dot{\hat{q}}_a & = & -D\hat{q}_a + E\frac{\chi}{x} \end{array} \right. \quad (4.40b)$$

$$\left\{ \begin{array}{lcl} \dot{x} & = & \frac{\chi}{x} . \end{array} \right. \quad (4.40c)$$

However, system (4.40) is not determined at $x = 0$. This problem can be solved by taking IC not at $t = 0$ and $x = 0$ but at a point very near to $t = 0$ and $x = 0$. To find this IC, we note that at the very first stage of capillary filling, the accumulated charge is small and has negligible effect on the filling phenomenon. Moreover, capillary filling without electric force involved is described by the equation system:

$$\left\{ \begin{array}{lcl} \dot{\chi} & = & \frac{\hat{F}_s}{C} - \frac{A}{C}\chi \end{array} \right. \quad (4.41a)$$

$$\left\{ \begin{array}{lcl} x\dot{x} & = & \chi . \end{array} \right. \quad (4.41b)$$

Table 4.1: Parameters used for numerical modelling.

Parameter	Symbol	Value	Unit
Surface tension	σ	71.97×10^{-3}	$\frac{\text{N}}{\text{m}}$
Dynamic viscosity	μ	1.003×10^{-3}	$\text{Pa} \cdot \text{s}$
Contact angle	θ	73.44	$^\circ$
Relative permittivity	ϵ	78	
Channel height	h	160×10^{-9}	m
Mass density	ρ_m	1.0×10^3	$\frac{\text{kg}}{\text{m}^3}$
Conductivity	λ	199×10^{-3}	$\frac{\text{S}}{\text{m}}$
Concentration	n_0	0.1	$\frac{\text{mole}}{\text{l}}$
Zeta potential	ζ	26	mV

The solution of (4.41) under ICs (4.38) is:

$$\begin{cases} \chi &= \frac{\hat{F}_s}{A} \left[1 - \exp\left(-\frac{A}{C}t\right) \right] \\ x &= \sqrt{\frac{2\hat{F}_s C}{A^2} \left[\exp\left(-\frac{A}{C}t\right) + \frac{A}{C}t - 1 \right]}. \end{cases} \quad (4.42a)$$

$$(4.42b)$$

In order to get the approximated ICs, a relatively small time interval (i.e., $t_0 = 10^{-9}$ second) is applied to (4.42a), and (4.42b). The IC for the accumulated charge of

$$\hat{q}_a(t_0) = 0 \quad (4.43)$$

is used as an approximated alternative.

To find the numerical solution, the parameters listed in Tab. 4.1 were used [103, 104]. With these parameters, the numerical solution of the equation system (4.40) was obtained by Matlab (MathWorks, USA), for various values of channel height and zeta potential.

4.2.9 Asymptotic Solutions

The system of non-linear ordinary differential equations (ODE) (4.37) can not be solved analytically. However, an asymptotic solution for $t \rightarrow \infty$ can be found. This method needs three variables which become stable as $t \rightarrow \infty$. The variables χ and u themselves have that property. The third variable chosen is:

$$\xi = \hat{q}_a x. \quad (4.44)$$

From (4.34c) and (4.44), the following relationships can be derived:

$$x = \frac{\chi}{\bar{u}} \quad (4.45)$$

$$\hat{q}_a = \frac{\xi}{\chi} \bar{u}. \quad (4.46)$$

Equation (4.40a) then becomes:

$$\dot{\chi} = \frac{\hat{F}_s}{C} - \frac{A}{C}\chi - \frac{B}{C}\xi. \quad (4.47)$$

Equation (4.40b) can be further transformed as:

$$\begin{aligned} \dot{q}_a &= -D\hat{q}_a + E\frac{\chi}{x} \\ \Rightarrow \dot{\hat{q}_a x} &= -D\hat{q}_a x + E\chi \\ \Rightarrow \dot{\hat{q}_a x} &= -D\xi + E\chi \\ \Rightarrow \dot{\hat{q}_a x} + \dot{x}\hat{q}_a &= -D\xi + E\chi + \dot{x}\hat{q}_a \\ \Rightarrow \frac{d}{dt}(\hat{q}_a x) &= -D\xi + E\chi + \bar{u}\hat{q}_a \\ \Rightarrow \dot{\xi} &= -D\xi + E\chi + \bar{u}\hat{q}_a. \end{aligned} \quad (4.48)$$

Substituting (4.46) into (4.48) leads to:

$$\dot{\xi} = -D\xi + E\chi + \frac{\xi}{\chi}\bar{u}^2. \quad (4.49)$$

From Eq. (4.40c), the acceleration $\ddot{u}$ can be derived as:

$$\begin{aligned} \dot{x} = \bar{u} &= \frac{\chi}{x} \\ \Rightarrow \dot{\bar{u}} &= \frac{\dot{\chi}x - \dot{x}\chi}{x^2} \\ \Rightarrow \ddot{u} &= \frac{\dot{\chi}x - \bar{u}\chi}{x^2}. \end{aligned} \quad (4.50)$$

Substituting (4.45) and (4.47) into (4.50) results in:

$$\ddot{u} = \left[\left(\frac{\hat{F}_s}{C} - \frac{A}{C}\chi - \frac{B}{C}\xi \right) \frac{\chi}{\bar{u}} - \bar{u}\chi \right] \frac{\bar{u}^2}{\chi^2}. \quad (4.51)$$

Writing (4.47), (4.49), and (4.51) together leads to the equation system:

$$\begin{cases} \dot{\chi} &= \frac{\hat{F}_s}{C} - \frac{A}{C}\chi - \frac{B}{C}\xi & (4.52a) \\ \dot{\xi} &= -D\xi + E\chi + \frac{\xi}{\chi}\bar{u}^2 & (4.52b) \\ \ddot{u} &= \left[\left(\frac{\hat{F}_s}{C} - \frac{A}{C}\chi - \frac{B}{C}\xi \right) \frac{\chi}{\bar{u}} - \bar{u}\chi \right] \frac{\bar{u}^2}{\chi^2}. & (4.52c) \end{cases}$$

It is necessary to look for the critical points in $(\chi, \xi, \bar{u})$ phase space to analyse the steady state. The critical point can be determined by looking for:

$$\left\{ \begin{array}{l} \dot{\chi} = 0 \\ \dot{\xi} = 0 \\ \dot{\bar{u}} = 0 . \end{array} \right. \quad \begin{array}{l} (4.53a) \\ (4.53b) \\ (4.53c) \end{array}$$

Then, the system of equations (4.52) becomes:

$$\left\{ \begin{array}{l} \frac{\hat{F}_s}{C} - \frac{A}{C}\chi - \frac{B}{C}\xi = 0 \\ -D\xi + E\chi + \frac{\xi}{\chi}\bar{u}^2 = 0 \\ \left[\left(\frac{\hat{F}_s}{C} - \frac{A}{C}\chi - \frac{B}{C}\xi \right) \frac{\chi}{\bar{u}} - \bar{u}\chi \right] \frac{\bar{u}^2}{\chi^2} = 0 . \end{array} \right. \quad \begin{array}{l} (4.54a) \\ (4.54b) \\ (4.54c) \end{array}$$

Substituting (4.54a) into (4.54c) leads to:

$$\left\{ \begin{array}{l} \frac{\hat{F}_s}{C} - \frac{A}{C}\chi - \frac{B}{C}\xi = 0 \\ -D\xi + E\chi + \frac{\xi}{\chi}\bar{u}^2 = 0 \\ -\frac{\bar{u}^3}{\chi} = 0 . \end{array} \right. \quad \begin{array}{l} (4.55a) \\ (4.55b) \\ (4.55c) \end{array}$$

Solving the system of equations (4.55) simultaneously results in:

$$\left\{ \begin{array}{l} \chi = \frac{D\hat{F}_s}{BE + AD} \\ \xi = \frac{E\hat{F}_s}{BE + AD} \\ \bar{u} = 0 . \end{array} \right. \quad \begin{array}{l} (4.56a) \\ (4.56b) \\ (4.56c) \end{array}$$

Because the velocity approaches zero at an infinite time $t \rightarrow \infty$, the critical point described by (4.56) is a stable point. A strict mathematical proof for this statement is more rigorous to achieve. However, several experimental assumptions can be made to derive the mathematical proof, as presented in Appendix B. Figure 4.2 demonstrates the stability of the critical point. The phase trajectory in Fig. 4.2 is generated numerically. The initial point is located utilizing the IC as in Tab. (4.38). The parameters as in Tab. 4.1 are used. The

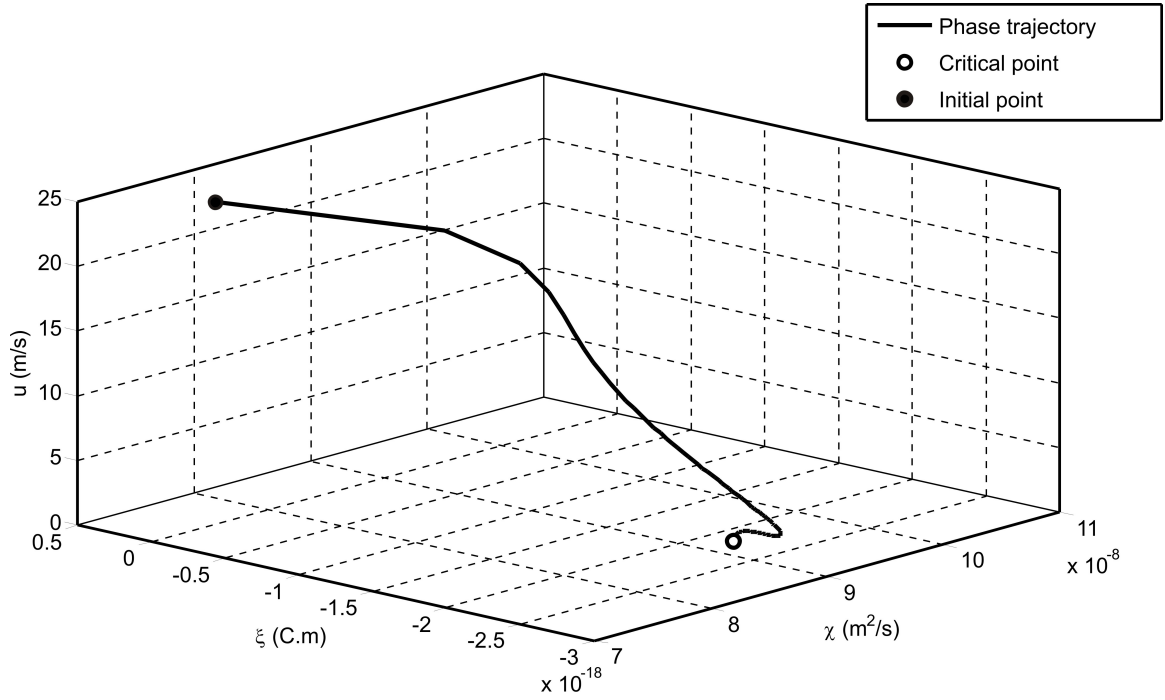


Figure 4.2: Phase trajectory in phase space.

critical point is located by Eq. (4.56). The movement of the trajectory toward the critical point shows that Eq. (4.56) practically indicates the asymptotic solution of (4.37).

Substituting Eq. (4.34c) into (4.56a) results in:

$$\begin{aligned}
 x\dot{x} &= \frac{D\hat{F}_s}{BE + AD} \\
 \Rightarrow xdx &= \frac{D\hat{F}_s}{BE + AD} dt \\
 \Rightarrow \frac{1}{2}x^2 &= \frac{D\hat{F}_s}{BE + AD}(t - t_0) .
 \end{aligned} \tag{4.57}$$

Using the IC (4.38a), the displacement can be determined as:

$$x = \left[\frac{2D\hat{F}_s}{BE + AD} t \right]^{1/2} . \tag{4.58}$$

The function (4.58) is the asymptote of the displacement as time approaches infinity $t \rightarrow \infty$, with the EDL effect.

For the purpose of comparison, the asymptote of the displacement without EDL effect is calculated similarly using the system of Eqs. (4.41):

$$x = \left[\frac{2\hat{F}_s}{A} t \right]^{1/2} . \tag{4.59}$$

Substituting the definitions $\hat{F}_s = 2\sigma \cos \theta$ and $A = 12\mu/h$ into (4.59) leads to:

$$x = \left[\frac{2\hat{F}_s}{A} t \right]^{1/2} = \left[\frac{\sigma \cos \theta h}{3\mu} t \right]^{1/2}. \quad (4.60)$$

Equation (4.58) can be written in the same form as (4.60), with the introduction of the apparent viscosity μ_a :

$$x = \left[\frac{2D\hat{F}_s}{BE + AD} t \right]^{1/2} = \left[\frac{\sigma \cos \theta h}{3\mu_a} t \right]^{1/2}. \quad (4.61)$$

The ratio between the apparent viscosity and the actual bulk viscosity is:

$$\frac{\mu_a}{\mu} = \frac{BE + AD}{2D\hat{F}_s} \frac{2\hat{F}_s}{A} = 1 + \frac{BE}{AD}. \quad (4.62)$$

Apparently, the EDL introduces an additional viscosity to the capillary filling phenomena of fluid in a nanochannel:

$$\frac{\Delta\mu}{\mu} = \frac{\mu_a - \mu}{\mu} = \frac{BE}{AD} = \frac{\Delta\mu}{\mu} = \eta \frac{\tanh\left[\frac{\kappa h}{2}\right] \left[\kappa h - 2 \tanh\left(\frac{\kappa h}{2}\right)\right]}{\left[1 + \frac{\zeta e}{kT} \frac{v_- - v_+}{v_+ + v_-} \frac{2 \tanh\left(\frac{\kappa h}{2}\right)}{\kappa h}\right] (\kappa h)^2}. \quad (4.63)$$

In a monovalent solution, the dimensionless parameter η is:

$$\eta = \frac{4\epsilon\epsilon_0 N_A \zeta^2 e^2}{\mu \Lambda_m kT} = 2 \frac{\zeta \kappa}{\mu} \frac{\bar{u}}{|\mathbf{E}|} \frac{\epsilon^2 \epsilon_0^2 \zeta \kappa N_A}{n_0 \Lambda_m} \frac{|\mathbf{E}|}{\bar{u}} = 2\eta_1 \eta_2 \quad (4.64)$$

where $\eta_1 = \frac{\zeta \kappa}{\mu} \frac{\bar{u}}{|\mathbf{E}|}$ is the ratio between electric force and viscous force, $\eta_2 = \frac{\epsilon^2 \epsilon_0^2 \zeta \kappa N_A}{n_0 \Lambda_m} \frac{|\mathbf{E}|}{\bar{u}}$ is the ratio between streaming current and conductive current.

Under normal conditions, i.e. $\zeta < 100$ mV and the temperature $T \approx 300$ K, the dimensionless parameter $\zeta e/kT$ has a value on the order of unity. For many common binary solutions, where the mobilities of ion species are the same, the ratio $\frac{v_- - v_+}{v_+ + v_-}$ reduces to zero. In extreme cases, $-1 < \frac{v_- - v_+}{v_+ + v_-} < 1$, this ratio does not change the trend of the ratio $\frac{\Delta\mu}{\mu}$ versus κh significantly, as illustrated in Fig. 4.3. Therefore, Eq. (4.63) can be further simplified to:

$$\frac{\Delta\mu}{\mu} = \eta \frac{\tanh\left[\frac{\kappa h}{2}\right] \left[\kappa h - 2 \tanh\left(\frac{\kappa h}{2}\right)\right]}{(\kappa h)^2}. \quad (4.65)$$

Figure 4.4 showed that formula (4.58) agrees well with the numerical result, and hence, can be used to predict the displacement of capillary filling in nanochannel, with an account

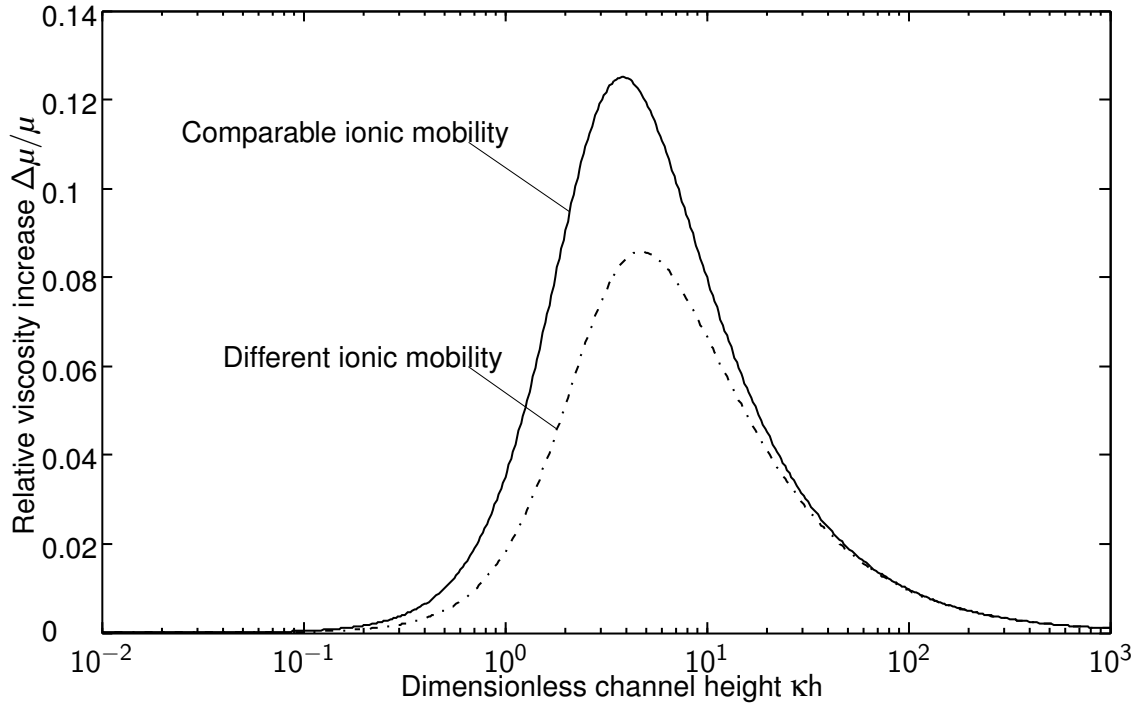


Figure 4.3: Dependence of $\Delta\mu/\mu$ ratio on the dimensionless channel height κh for two different cases (Dashed line: mobility of two species of ion is almost the same; Solid line: mobility of anion is much higher than that of cation).

to the EDL effect. The numerical solution of equation:

$$\left. \frac{d}{dx} \frac{\tanh\left(\frac{x}{2}\right) \left[x - 2 \tanh\left(\frac{x}{2}\right)\right]}{x^2} \right|_{x=\kappa h} = 0 \quad (4.66)$$

showed that the maximum of each curve is reached at $\kappa h \approx 3.8$

Figure 4.5 shows the ratio $\Delta\mu/\mu$ with respect to normalized channel height κh with various values of η . Some experimental data reproduced from literature are also plotted for comparison.

According to Eq. (4.65), the dimensionless channel height κh is determined by both the channel height and the electrolyte concentration. At room temperature, the Debye length κ^{-1} ranges from several nanometers to a theoretical maximum of several hundreds nanometers for pure water. Therefore, it is necessary to fabricate channels with height in nanoscale in order to observe the electroviscous effect. With a specific channel height, there is one optimum concentration at which the electroviscous effect is most significant. Diluted or concentrated solution (relative to such optimum concentration) gives a lower increase in viscosity, as illustrated in Fig. 4.6. Figure 4.7 shows that if the channel height

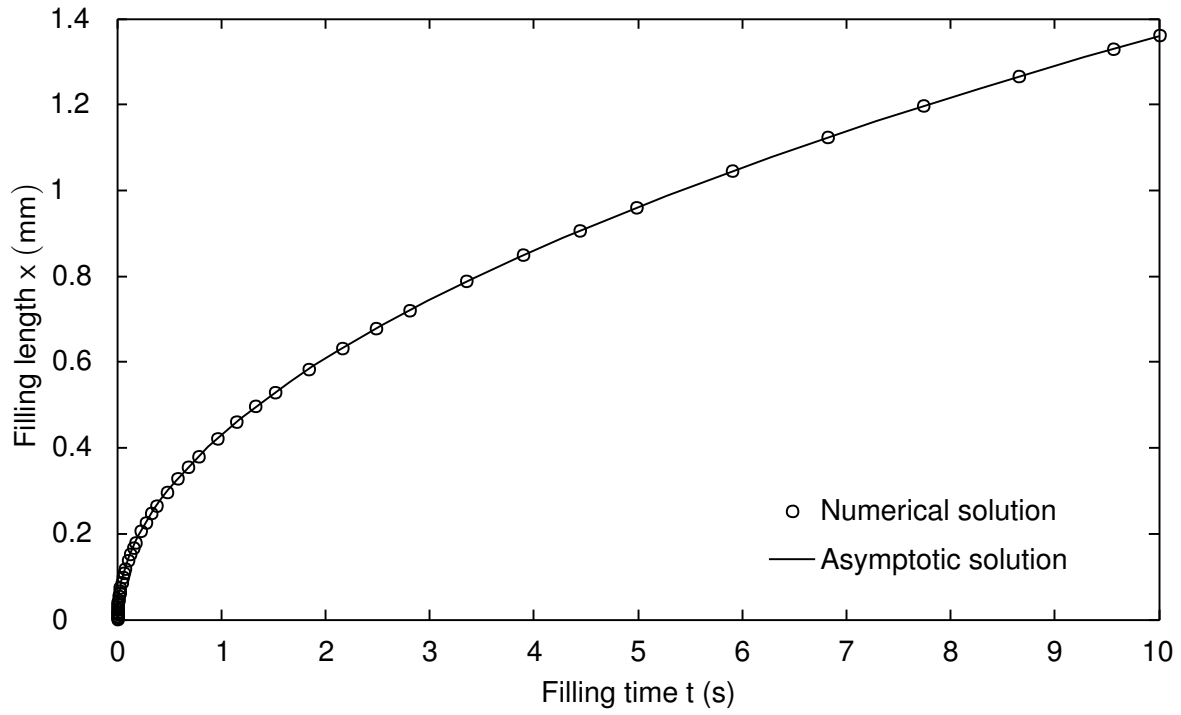


Figure 4.4: Capillary filling displacement with 30 nm channel height, 26 mV zeta potential and the asymptotic solution.

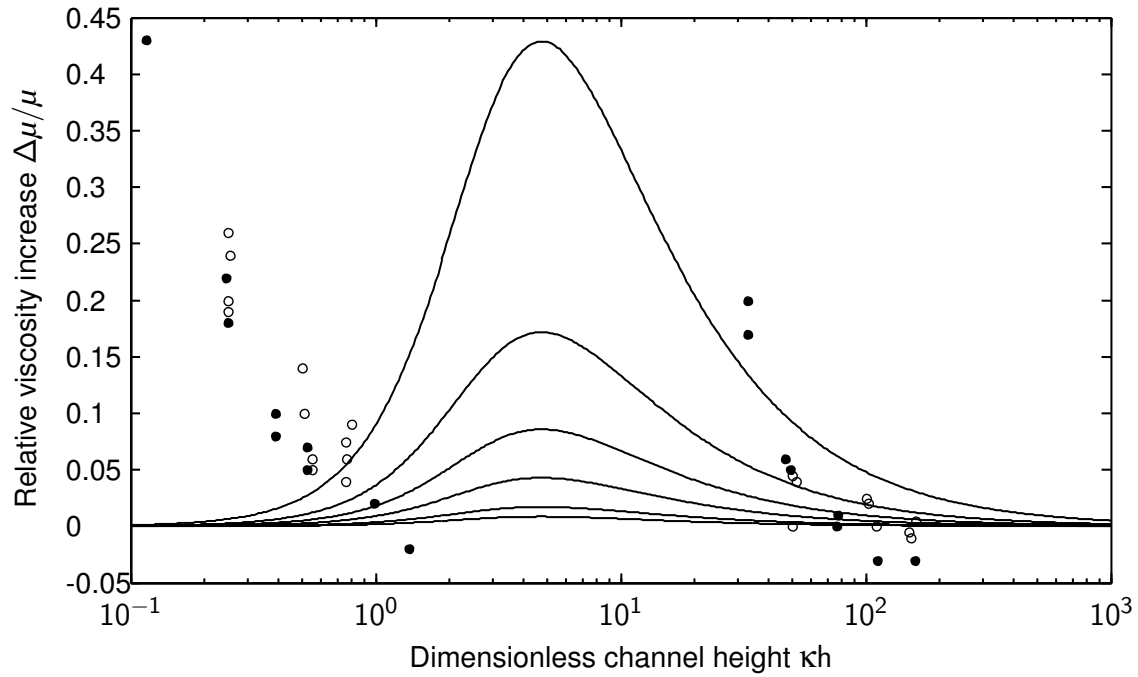


Figure 4.5: Ratio $\Delta\mu/\mu$ with respect to normalized channel height κh with $\eta=0.1, 0.2, 0.5, 1, 2, 5$ (solid lines from below). Open data points are from (Tas et al., 2004). Close data points are from (Persson et al., 2007).

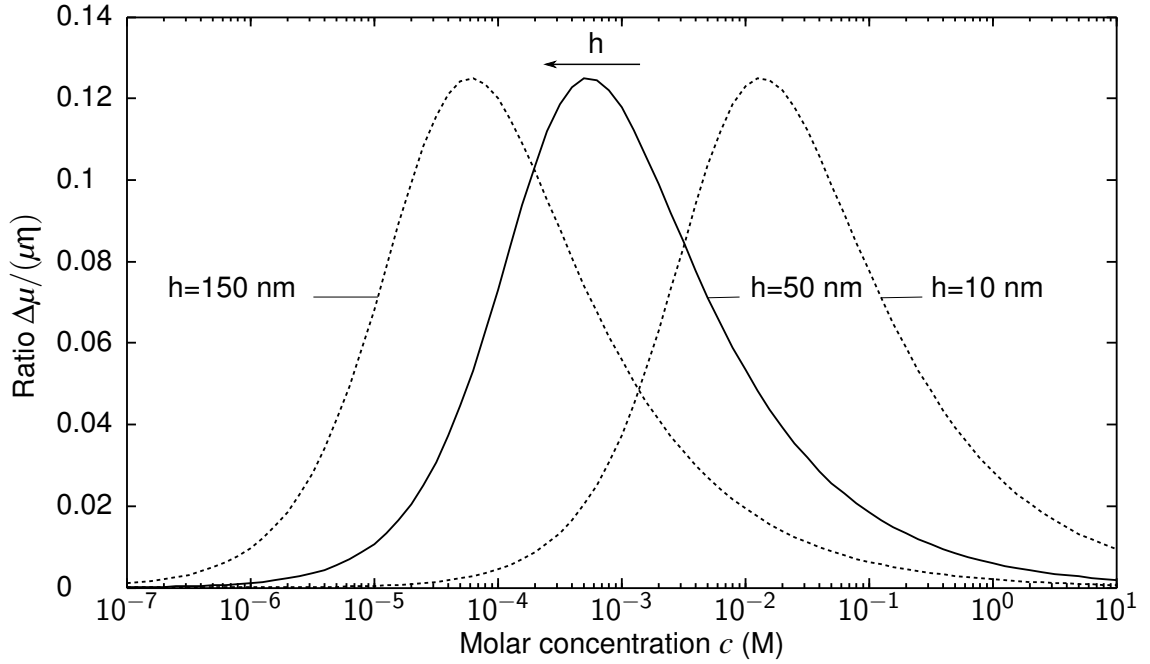


Figure 4.6: Ratio $\Delta\mu/(\mu\eta)$ versus concentration at different channel heights.

is on the order of tens to hundreds of nanometers, the solution must be very dilute (e.g., $10^{-6}M$) to reach the maximum apparent viscosity. At a higher concentration, the apparent viscosity simply increases with the decreasing channel height.

In Fig. 4.8, the ratio $\Delta\mu/\mu\eta$ with respect to normalized channel height κh is plotted in comparison with the corresponding ratio of the linearized model reported previously [9], the results showed a close agreement between the two models.

Generally, electroviscous effect is the coupling between electrokinetic and dynamic fluid flow in the nanochannel. The model described here attempts to explain what happens during capillary filling. In a general perspective, the model determines which phenomena involve in the filling process, and describes these phenomena in term of the parameters of Eq. (4.58) as follows: $\hat{F}_s$ represents the surface force, A evaluates the contribution of actual viscosity, B determines the contribution of longitudinal electric interaction through charge density distribution, C describes the inertia force, D evaluates the contribution of ions mobilities and E describes the coupled effect between pressure-driven flow and ions redistribution. For the sake of readability, simplified models were used to describe the phenomena. However, this approach is also applicable to more complicated cases, which merely lead to the modification in value of the parameter $\hat{F}_s$, A , B , C , D , and E , without

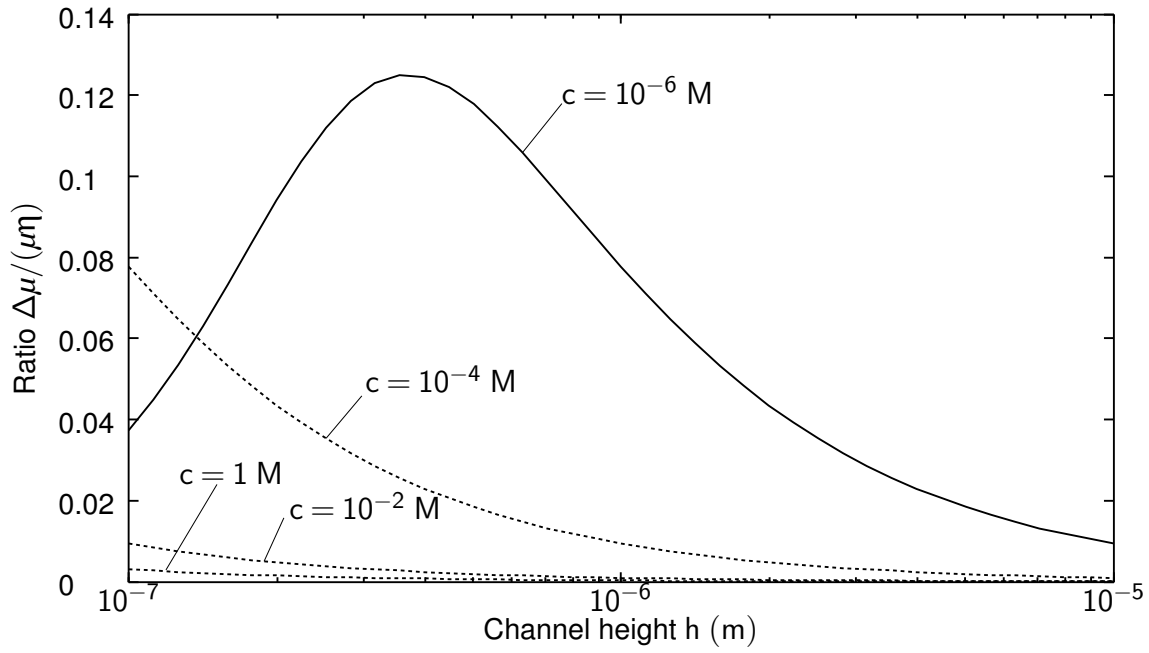


Figure 4.7: Ratio $\Delta\mu/(\mu\eta)$ versus channel height at different concentrations.

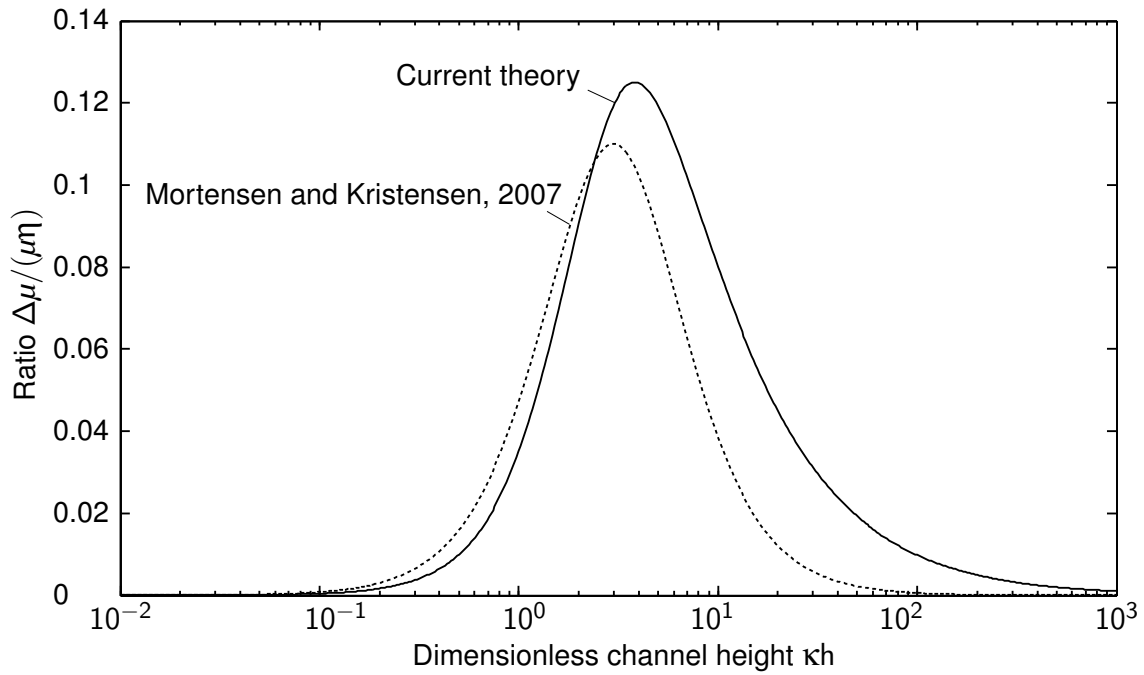


Figure 4.8: Ratio $\Delta\mu/(\mu\eta)$ versus normalized channel height compare to Mortensen and Kristensen, 2007.

the necessity to rebuild the whole derivation. For each specific case, these parameters can be obtained analytically, numerically, or even experimentally.

The absent of C in the final formula (4.58) of asymptotic solution shows that the effect of inertia force in nanochannels is negligible, because the volumetric effect such as inertia force becomes insignificant. For that reason, in subsequent analyses of this thesis, the inertia force is eliminated. Among other parameters, increasing $\hat{F}_s$ and D increases the filling speed while increasing the absolute values of A , B , and E reduces the filling speed. Figure 4.9 illustrates the change in filling function with respect to the changes in the parameters $\hat{F}_s$, A , B , C , D , and E .

4.3 Experiments

Nanochannels fabricated by 1 mm thick PMMA plate using hot embossing and thermal bonding similar to those reported in Chapter 3 with channel height of 220 nm were used to perform capillary filling experiment. Figure 4.10 shows the setup of the capillary filling experiment. Deionized water (DIW), solutions of water and sodium chloride (NaCl) with different concentration (0.01M and 0.1M) and isopropanol (IPA) 99% were introduced into the access holes and then fill in the nanochannels under the influence of capillary force. Horibe et al. [105] reported on the change of surface tension of NaCl solution as a function of concentration and temperature. Sawamura et al. [106] investigated the relation between pressure, temperature and concentration of NaCl solution and the dynamic viscosity. However, because low-concentration NaCl solutions were used in this experiment, the variations of those parameters from pure water are negligible (less than 1%). Gibbs and Young equation establishes the relation between the contact angle and the surface energies. In this experiment, it is assumed that low concentration of NaCl does not affect the surface energies, and therefore, does not change the contact angle. As a result, the surface tension, contact angle, and viscosity of water was used for NaCl solutions with concentrations of 0.1M and 0.01M. The properties at 25°C of NaCl solutions and IPA 99% are provided in Tab. 4.2, [105, 107, 108]. The filling process was observed under an upright microscope (Nikon, Japan) and captured in form of 640px $\times$ 480px grey scale video files by a CCD camera (Pulnix TM6701AN, Leutron Vision, USA) with a deterministic frame rate. Due

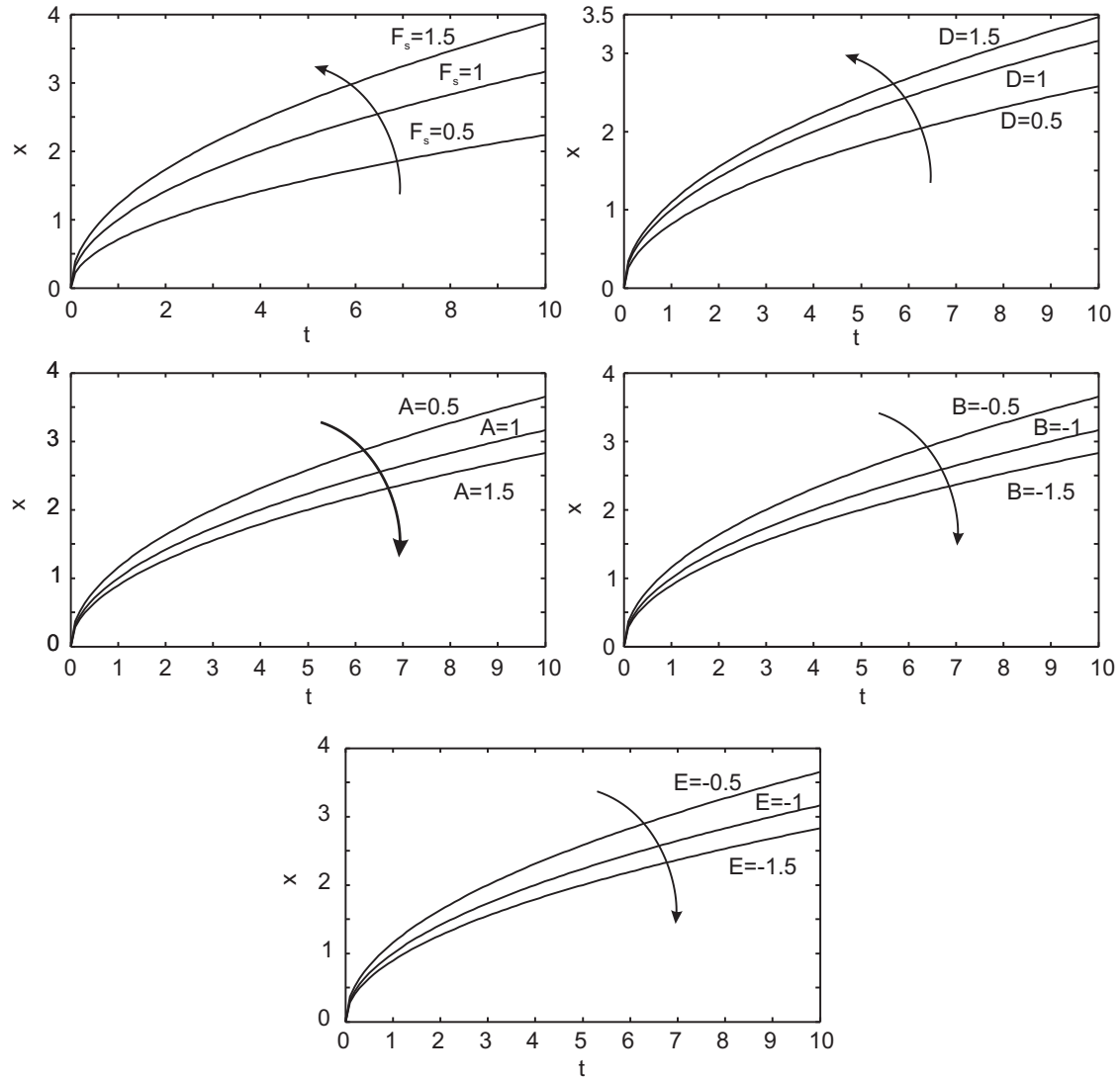


Figure 4.9: Change in filling distance as a function of time, with respect to the changes in the parameters: (a) $\hat{F}_s$ presents the surface force; (b) D presents the contribution of ions mobilities; (c) A presents the contribution of actual viscosity; (d) B presents the contribution of longitudinal electric interaction through charge density distribution; (e) E represents the contributions the coupled effect between pressure-driven flow and ions redistribution. Increasing in $\hat{F}_s$ and D increases the filling speed. Increasing in A reduces the filling speed. Increasing in absolute values of B , and E reduces the filling speed. The sign of B and E is opposite to that of zeta potential

Table 4.2: Properties of fluids used in capillary filling.

Fluid	σ (mN/m)	θ (Degree)	μ (mPa · s)
NaCl 0.01M	72.0	73.4	1.00
NaCl 0.1M	72.0	73.4	1.00
DIW	72.0	73.4	1.00
IPA 99%	23.0	0.00	1.96

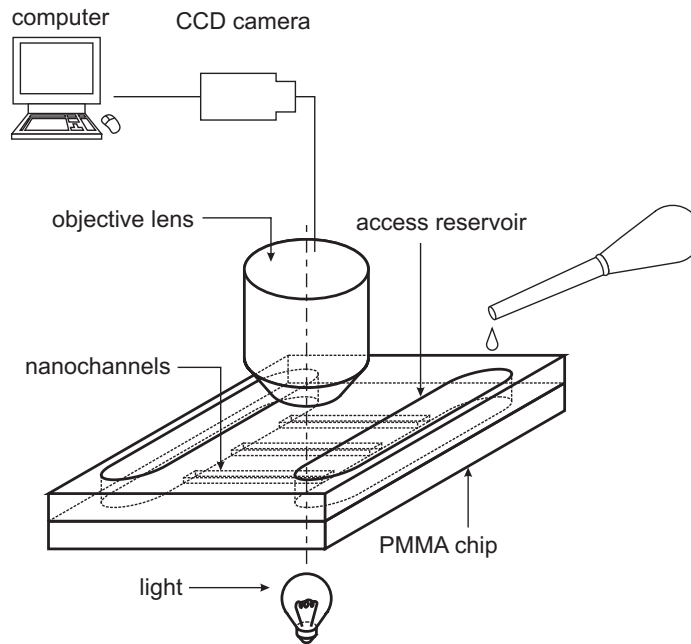


Figure 4.10: Experimental setup.

to the difference in the index of refraction between the fluid and PMMA, the filled areas of the channel appear darker in the images. Figure 4.11 shows a typical image captured for the analysis. The filling distances were measured by the image processing package of Matlab (Mathworks, USA). First, grey scale images of all channels in the chip were extracted. Subsequently, grey scale images were converted into black and white binary images using an appropriate threshold, so that the filled areas appear black while the unfilled areas appear white. Morphological image closing operator with disk-shaped structuring element was applied on the images to clean up the noise. Blob analysis algorithms were used to determine the length of the filling distance in pixels. The filling distances in pixels were then converted into actual length by comparing with the length of a scale imprinted on the chip surface. The filling distance versus time function was recorded and analysed. Figure 4.12 shows the measured filling distance versus time in a group of similar channels of the same chip. The images show the variations in filling distance. These variations were caused by uncertainty in fabrication process and possible nanoscale effects such as bubble formation in the channel.

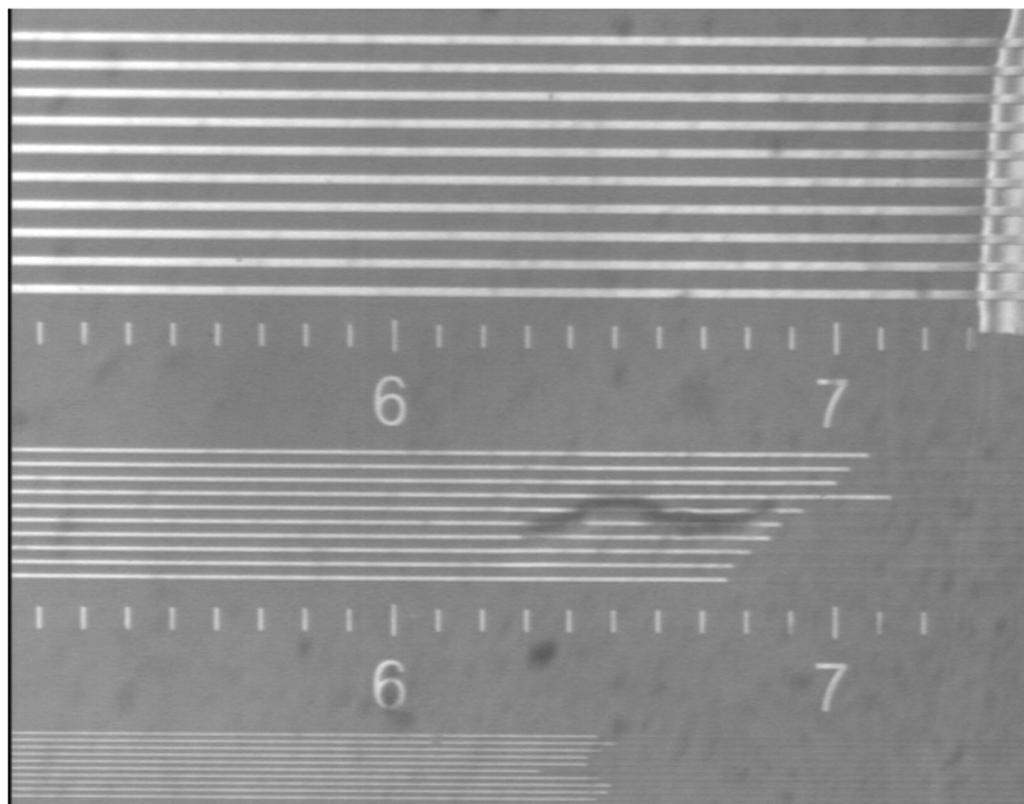


Figure 4.11: An image captured during the filling process.

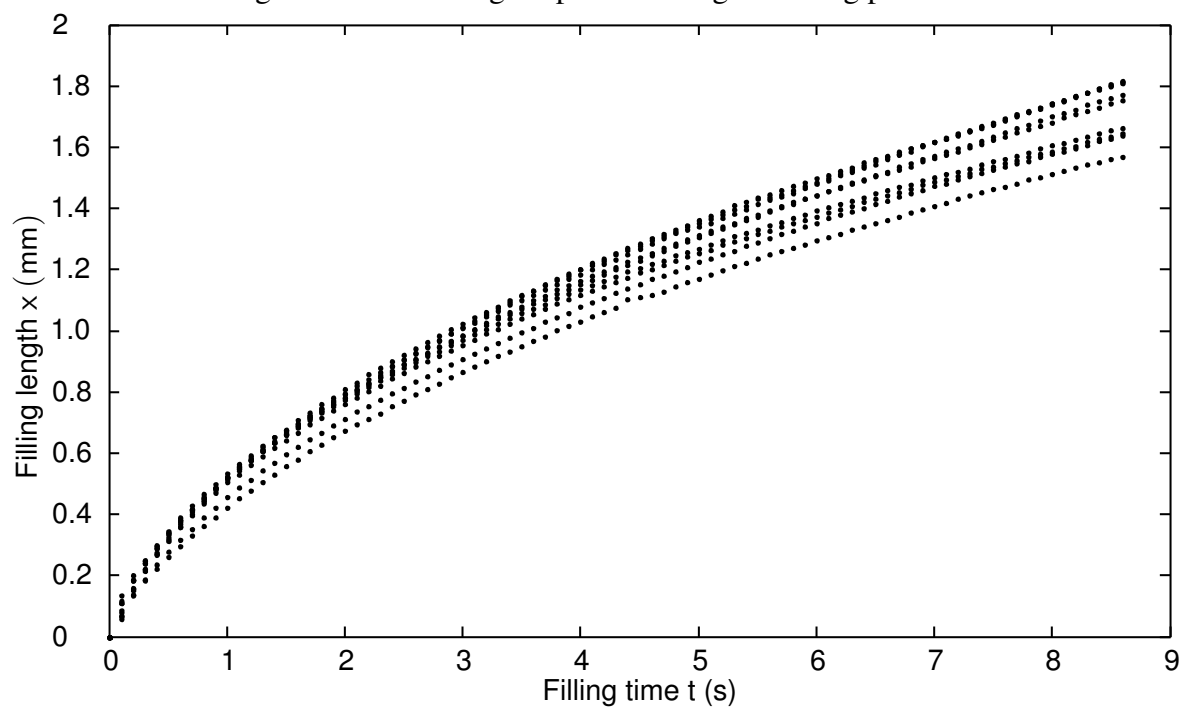


Figure 4.12: Filling distance versus time recorded in channels of 220 nm height, 4 μm width filled with 0.1 M NaCl.

4.4 Results and Discussions

Plots of the square of the experimental capillary filling distance time reveal that capillary filling qualitatively follows Washburn formula:

$$x \propto \left[\frac{\sigma \cos \theta h}{3\mu} t \right]^{1/2} \quad (4.67)$$

except the initiation region, where the filling speed seems to be lower than expected. Therefore, an entrance resistance may exist due to the ambiguous geometry at the entrance of the polymeric nanochannels. Equivalent channel length of this resistance is derived by extrapolation method, the value gives the maximum correlation between square of position and time is accepted. Let $\mathbf{x}$ and $\mathbf{t}$ be filling length and time data vectors, the value of equivalent entrance length L_e is the root of Eq. (4.68):

$$\frac{d}{dL_e} \text{corr}((\mathbf{x} + L_e)^2, \mathbf{t}) = 0 \quad (4.68)$$

where $\text{corr}(\mathbf{x}, \mathbf{y})$ is the correlation function between two data vectors $\mathbf{x}$ and $\mathbf{y}$, indicates the linear relationship between two random variables, defined by the covariance of $\mathbf{x}$ and $\mathbf{y}$ divided by the products of two standard deviations of $\mathbf{x}$ and $\mathbf{y}$. The value of correlation function is within $[-1, +1]$ range, with $+1$ value indicates increasing relationship while -1 value indicates decreasing relationship. The corrected filling length is $\mathbf{x}' = \mathbf{x} + L_e$. Linear regression is used to determine the Washburn coefficient. Corrected time data vector $\mathbf{t}'$ was also found by linear regression so that the condition $x = 0$ at $t = 0$ satisfies. Figure 4.13 shows one typical filling result with and without entrance resistance.

Entrance resistance corrected plots of the square of the experimental capillary filling distance versus time are shown in Fig. 4.14 for the case of 1×10^{-3} M NaCl solution filling in nanochannels of 200-nm depth, 2- μm width. This figure also presents the comparison between the filling predicted by applying electroviscous effect as in current theory and experimental data. Similar results for NaCl solutions, isopropanol, and DIW in various channel sizes are presented in Appendix C. These results show three important points. Firstly, the highly linearity of the experimental data points suggests that the filling qualitatively follow Washburn's theory. Secondly, for electrolytic solutions, the experimental filling speed reduction is one to two orders higher than that predicted by electroviscous

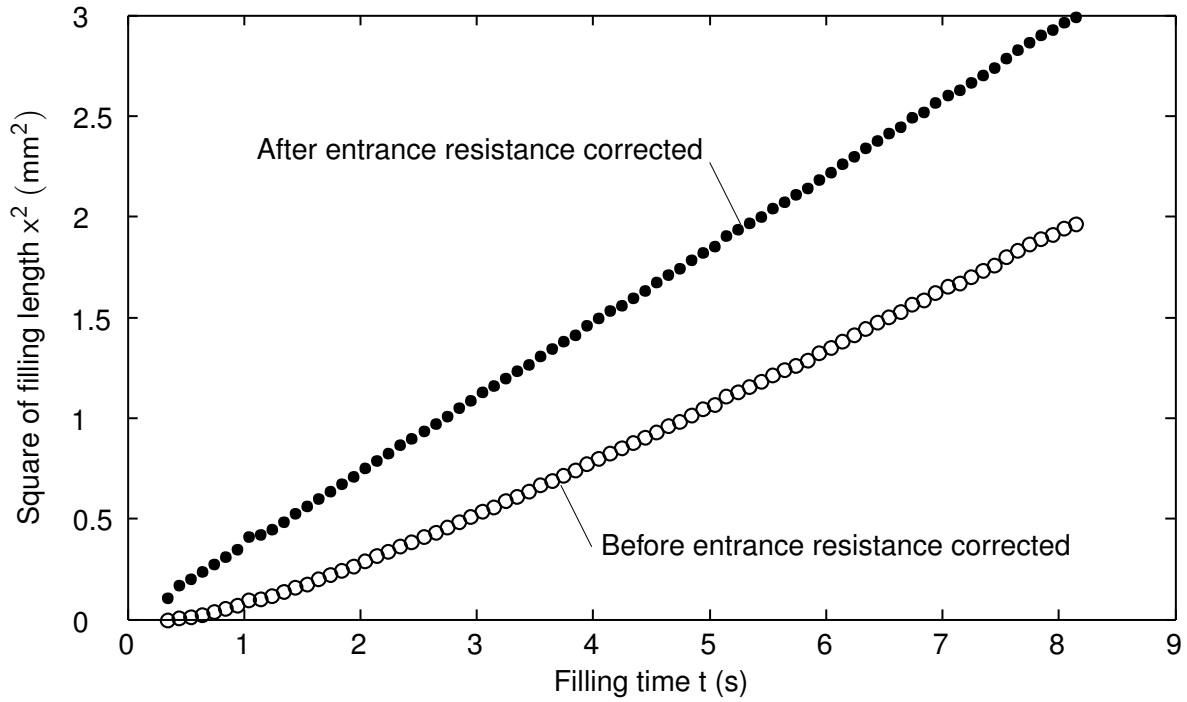


Figure 4.13: A typical experimental result with and without entrance resistance correction. White circles represent filling distances measured from the entrances of the channels. Black dots present filling distances with entrance resistance corrected.

effect. Thirdly, the filling speed reduction also exists with the same order even for very weak electrolytic or non-electrolytic liquids like DIW or isopropanol. These liquids are supposed to show very little or negligible electroviscous effect. These observations are also consistent with previous experimental data, presented in Fig. 4.5. These observations suggest that electroviscous effect is not the only cause of the filling speed reduction.

The filling speed reduction is expressed in term of a lower Washburn coefficient

$$a = \frac{\sigma \cos \theta h}{3\mu} \quad (4.69)$$

in comparison to the classical Washburn's theory. This reduction in Washburn coefficient can be further broken down to an increase in apparent viscosity, a reduction in apparent surface tension, or an increase in the effective contact angle. The significance of these parameters are discussed hereafter.

Various investigations reported the reduction in the speed of flow in pressure driven flow and capillary filling [9, 21, 109, 110]. Electroviscous effect is usually addressed as the cause of such reduction in the speed of flow, which is expressed by an apparent increase in viscosity. Table 4.3 presents the ratio between the apparent viscosities found during

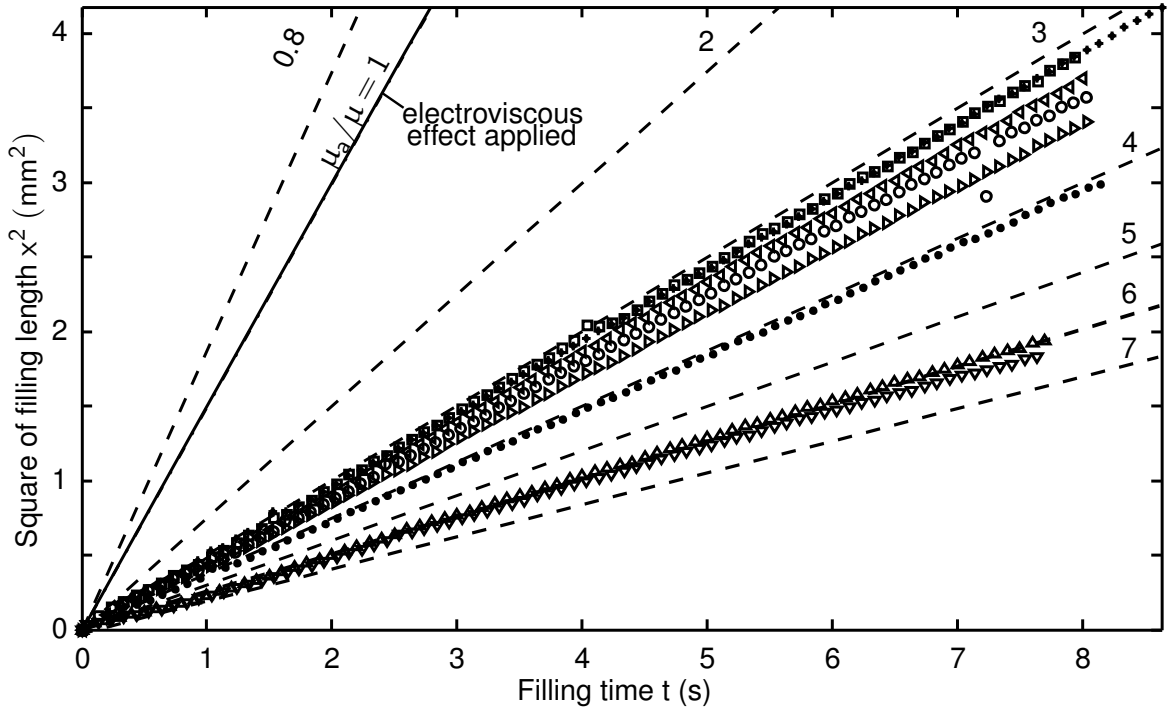


Figure 4.14: Square of filling length of 0.001 M NaCl in nanochannels of 220 nm depth, 2 μm width.

the experiment to the standard values of the fluids. These values are summarized from the results presented in the graphs in Appendix C. The values of viscosity ratio reported in Tab. 4.3 are higher than that predicted by the theoretical model presented in Section 4.2. With NaCl solution, the dimensionless parameter $\eta \approx 0.5$, substitution into Eq. (4.65) gives a maximum increase in apparent viscosity of not more than 5%, far less than those measured as shown in Tab. 4.3. This deviation again clarifies that the electroviscous effect is not the only cause of the speed reduction in capillary filling.

There are reports on the formation of air bubbles during the filling process [36,42]. A fraction of energy is stored in term of surface energy of the air bubbles; hence, less energy transfers to kinetic energy of the fluid column, which leads to reduction in filling speed. The energy loss to the formation of air bubbles is equivalent to an apparent reduction in surface tension. Tab. 4.4 presents the apparent surface tension σ_a that fit the experimental filling distance for different kinds of fluid, compare to bulk materials surface tension. The apparent surface tension is derived with bulk values of contact angle and viscosity of each materials, Tab. 4.2.

Table 4.3: Ratio between apparent viscosity to standard value for different fluids and channel geometries.

Fluid	Channel width (μm)	Viscosity Ratio	
		Mean	Std dev
NaCl 0.01M	2	4.05	1.26
NaCl 0.01M	5	3.08	0.43
NaCl 0.01M	8.8	2.28	0.22
NaCl 0.1M	2	4.38	0.35
NaCl 0.1M	5	3.88	0.51
NaCl 0.1M	8.8	3.19	0.15
DIW	2	3.36	0.14
DIW	5	2.84	0.13
IPA 99%	2	2.91	0.03
IPA 99%	5	2.79	0.12
IPA 99%	8.8	2.84	0.16

Table 4.4: Apparent surface tension compares to standard value for different fluids and channel geometries.

Fluid	Channel width (μm)	σ	σ_a
		(mN/m)	(mN/m)
NaCl 0.01M	2	72.0	17.8
NaCl 0.01M	5	72.0	23.4
NaCl 0.01M	8.8	72.0	31.6
NaCl 0.1M	2	72.0	16.4
NaCl 0.1M	5	72.0	18.6
NaCl 0.1M	8.8	72.0	22.6
DIW	2	72.0	21.4
DIW	5	72.0	25.4
IPA 99%	2	23.0	7.90
IPA 99%	5	23.0	8.24
IPA 99%	8.8	23.0	8.10

Table 4.5: Apparent contact angle compares to standard value for different fluids and channel geometries.

Fluid	Channel width (μm)	θ (Degree)	θ_a (Degree)
NaCl 0.01M	2	73	85.9
NaCl 0.01M	5	73	84.6
NaCl 0.01M	8.8	73	82.6
NaCl 0.1M	2	73	86.2
NaCl 0.1M	5	73	85.7
NaCl 0.1M	8.8	73	84.7
DIW	2	73	85.0
DIW	5	73	84.1
IPA 99%	2	0	69.9
IPA 99%	5	0	69.0
IPA 99%	8.8	0	69.4

Figure 4.15 shows the air bubbles formation observed during the experiment with 99% IPA and also the irregularity of the advancing meniscus, which are certainly the cause of difference between experimental and theoretical results by alternating the effective contact angle of the meniscus. Table 4.5 shows the apparent contact angle θ_a that fits the experimental filling distance derived with bulk values of contact angle and surface tension, as in Tab. 4.2. In order to observe the electroviscous effect, it is essential to eliminate, or quantitatively evaluate other factors contributing to speed reduction, such as air bubbles formation.

The formation of small solid blockages in the channel during the fabrication and the experiments can also cause the reduction in filling speed. The variation of filling speed shown in Fig. 4.12 demonstrates the effect of uncertainty from the fabrication. The formation of solid blockages was also observed after the filling experiment. The blockages appeared under the microscope as fractal-like structures. AFM analysis confirmed that they are solid protrusions that block the whole height of the channels. Figure 4.16 shows the microscopic image of the blockages forming after the filling of IPA 99% in PMMA nanochannels while Fig. 4.17 presents the AFM analysis of those blockages found in the channels and on the cap after disassembling the chip. The shapes of these blockages suggest that they were formed by crystallization of substances diluted in the fluid. Although the formation mechanism of these blockages is still unknown, the filling speed may reduce if the formation started during the filling process, especially if it induces the formation of air bubbles.

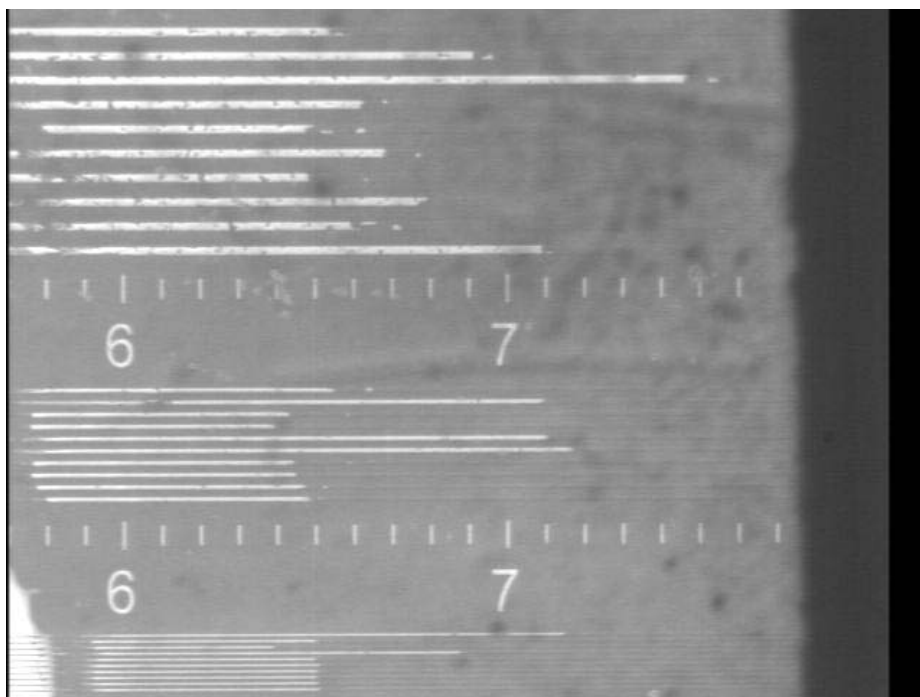


Figure 4.15: Image captured during capillary filling process with 99% IPA. Air bubbles formation was observed at large and medium channel.

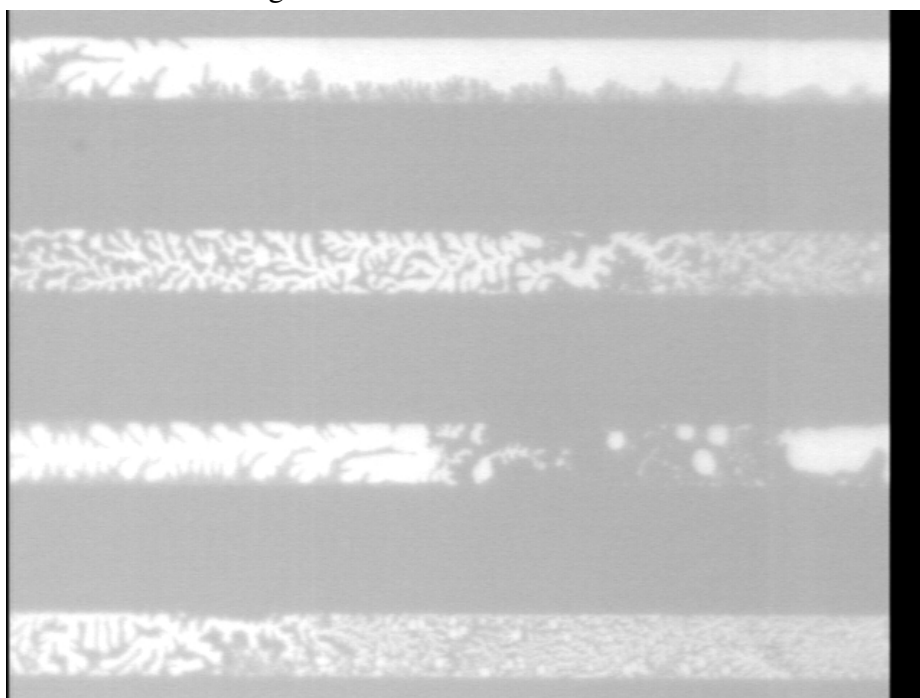


Figure 4.16: Microscopic image of blockages formed after the capillary filling of IPA 99% in 220-nm-height PMMA nanochannels.

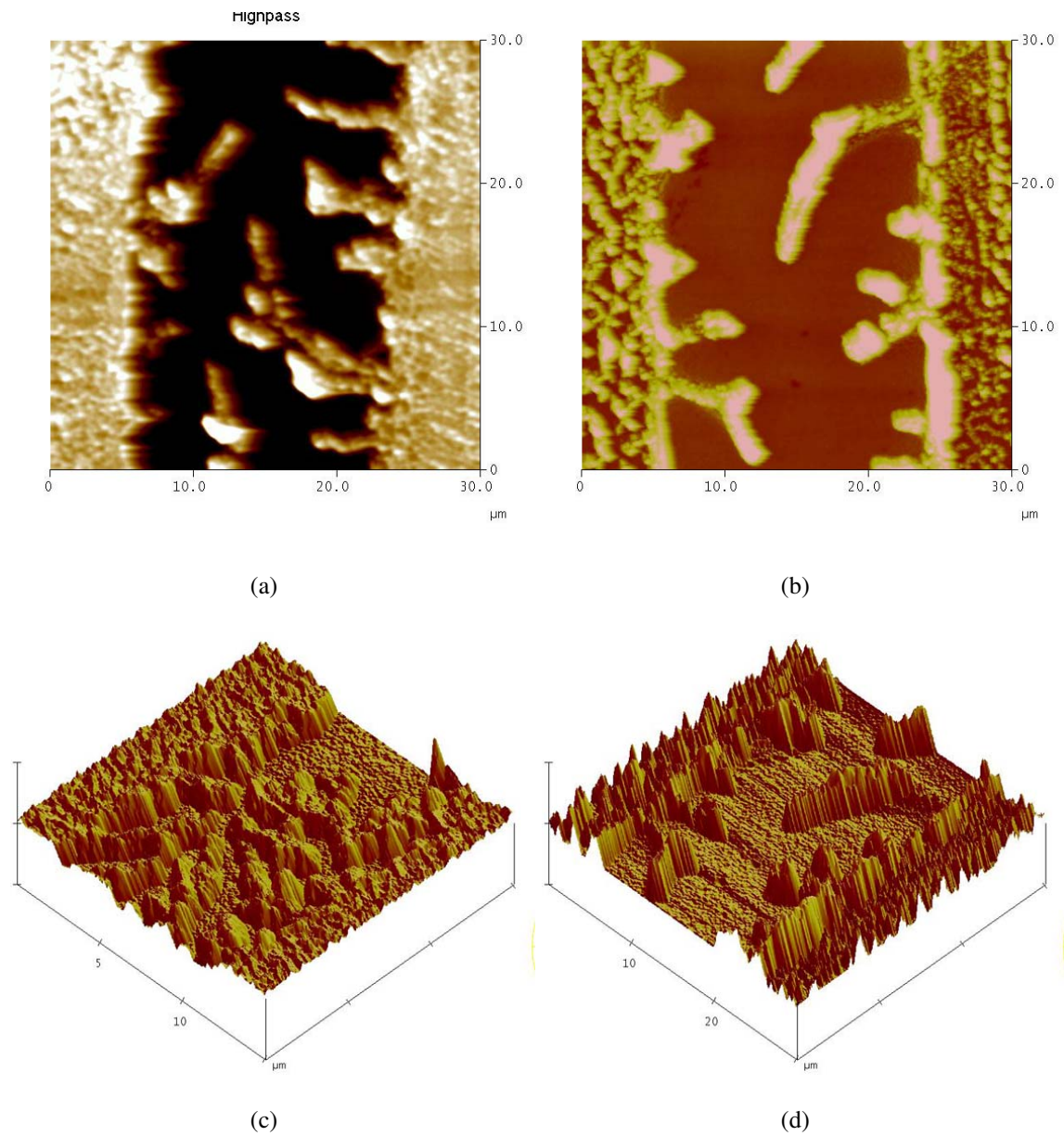


Figure 4.17: AFM analysis of the blockages forming after the filling of IPA 99% in 220-nm-height PMMA nanochannels: (a) top view of the blockages in the channel; (b) top view of the blockages on the cap piece; (c) 3D images of the blockages in the channel; (d) 3D images of the blockage on the cap piece.

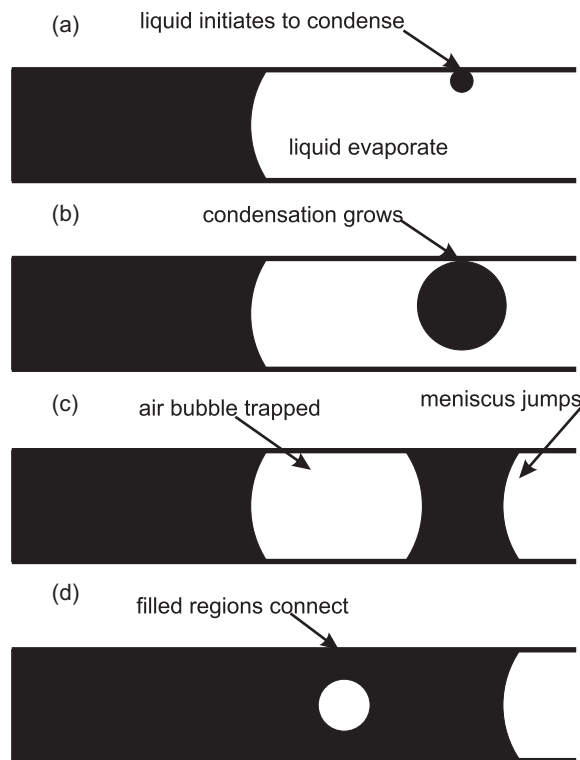


Figure 4.18: Condensation of liquid in front of the meniscus leads to the formation of air bubbles and the forward jump of the meniscus: (a) The condensation initiate at a distance from the meniscus; (b) The condensation region grows larger; (c) The air bubble is trapped, the formation of a new meniscus is observed as a sudden forward jump of the meniscus; (d) The filled regions connect, trapping the spherical air bubble, which gradually reduces its size.

A combination of evaporation, condensation and air bubbles formation is also noticeable. The liquid evaporating from the meniscus condenses in the region in front of the meniscus. The initiation of condensation depends on the fluctuation of temperature and the surface finish of the channel walls. The condensation region grows larger trapping the air in the vacancy. New meniscus forms eventually lead to the sudden forward jump of the meniscus as described in [42]. At the same time, an air bubble forms in the filled region. The process is illustrated in Fig. 4.18. The air bubbles in large channel areas of Fig. 4.15 are observed to form in this manner.

Chapter 5

Filling in Closed-End Nanochannels

5.1 Background

The current chapter investigates the importance of gas absorption into liquid. This phenomenon was neglected in all previously reported works on liquid transport in nanochannels. In this chapter, capillary filling process in closed-end nanochannels was experimentally investigated. In contrast to closed-end microchannels, the nanoscale channel height allows a relatively slow filling speed so that the whole process can be investigated in details. A similar problem in microchannels has been investigated by Pesse et al. [56]. The authors performed filling experiments in rectangular-cross-section, closed-end microchannels with lengths ranging from 50 to 150 μm . The experimental results were compared to the theory. However, due to the random appearance of liquid in the microchannels, the experimental data did not fully fit to the theoretical model. In the present work, quantitative measurements of filling lengths versus time were obtained for ethanol and isopropanol to avoid the problems of water in closed-end microchannels as reported previously by Pesse et al. Experiments were also carried out with DIW to confirm that the same behaviour also exists in nanochannels.

The behaviour of menisci during the filling process and the formation of air bubbles were recorded and qualitatively investigated. A theoretical model is developed based on the absorption and diffusion of gas in liquid to predict the position of the meniscus. In the model suggested by Pesse et al., only absorption and diffusion of air in liquid was consid-

ered, due to the relatively low Laplace pressure in microchannels compared to atmospheric pressure. In nanochannels, the Laplace pressure is high enough to cause significant air compression. Therefore, air compression plays an important role in the final result. Moreover, while the model used by Pesse et al. assumed diffusion in a semi-infinite medium, the present model considers the variation of filling length in the diffusion process.

5.2 Theoretical Analysis

There are three forces acting on the liquid in the nanochannels. The surface force F_s due to the surface tension is the driving force for the whole filling process. The viscous force F_v limits the filling speed while the force F_p caused by the pressurized air trapped in the nanochannels acts against the filling process. Because the inertia force is negligible in nanoscale, the force balance leads to:

$$F_s + F_v + F_p = 0 . \quad (5.1)$$

The formulae of these forces in a closed-end planar nanochannel of the height h , the width w ($h \ll w$), and the length L is:

$$F_s = 2w\sigma \cos \theta \quad (5.2)$$

$$F_v = -\frac{12\mu u}{h}wx \quad (5.3)$$

$$F_p = -hw(p - p_0) \quad (5.4)$$

where σ is the surface tension of the fluid, θ is the contact angle between the fluid and the wall of the nanochannels, μ is the dynamic viscosity of the fluid, u is the filling speed, x is the filling length, p is the pressure of the trapped air, p_0 is the initial pressure of the trapped air volume. If the experiment is carried out in standard at atmospheric condition, p_0 is the atmospheric pressure. The formulae above are valid with the assumptions that the system is isothermal and the filling velocity profile is parabolic across the channel height.

With negligible gas absorption, e.g. in a channel of micro scale or larger, the mass of air trapped in the channel is conserved. The pressure force F_p is then:

$$F_p = -hw p_0 \left[\frac{L}{L-x} - 1 \right] = -hw p_0 \frac{x}{L-x} . \quad (5.5)$$

Equation (5.1) leads to:

$$\begin{aligned} 2\sigma_w \cos \theta &= \frac{12\mu u}{h} wx + hw p_0 \frac{x}{L-x} \\ \Rightarrow u = \frac{dx}{dt} &= \frac{h\sigma \cos \theta}{6\mu x} - \frac{h^2 p_0}{12\mu(L-x)} . \end{aligned} \quad (5.6)$$

Equation (5.6) can be written in dimensionless form:

$$\begin{aligned} \frac{dx^*}{dt^*} &= \frac{1}{x^*} - \frac{\alpha}{1-x^*} \\ \Rightarrow dt^* &= \frac{x^* - x^{*2}}{1 - (1+\alpha)x^*} dx^* \\ &= \left[\frac{1}{1+\alpha} x^* - \frac{\alpha}{(1+\alpha)^2} - \frac{\alpha}{(1+\alpha)^2} \frac{1}{(1+\alpha)x^* - 1} \right] dx^* \end{aligned} \quad (5.7)$$

where x^* , t^* and α are dimensionless parameters:

$$x^* = \frac{x}{L} \quad (5.8)$$

$$t^* = \frac{t}{2\tau_{\text{capillary}}} \quad (5.9)$$

$$\alpha = \frac{hp_0}{2\sigma \cos \theta} . \quad (5.10)$$

The characteristic time $\tau_{\text{capillary}} = 3\mu L^2 / h\sigma \cos \theta$ is the time needed for to fully fill an open channel of a length L by capillary filling. The parameters α is the ratio between the force caused pressure of trapped gas and the surface force. With the initial condition $t^*(0) = 0$ for any $x_0^* < \frac{1}{1+\alpha}$, (5.7) leads to:

$$\begin{aligned} t^*(x_0^*) &= \int_0^{x_0^*} \frac{1}{1+\alpha} x^* dx^* - \int_0^{x_0^*} \frac{\alpha}{(1+\alpha)^2} dx^* - \frac{\alpha}{(1+\alpha)^2} \int_0^{x_0^*} \frac{1}{(1+\alpha)x^* - 1} dx^* \\ &= \frac{x_0^{*2}}{2(1+\alpha)} - \frac{\alpha x_0^*}{(1+\alpha)^2} - \frac{\alpha}{(1+\alpha)^3} \ln[1 - (1+\alpha)x_0^*] . \end{aligned} \quad (5.11)$$

Replacing x^* by x_0^* results in:

$$t^*(x^*) = \frac{x^{*2}}{2(1+\alpha)} - \frac{\alpha x^*}{(1+\alpha)^2} - \frac{\alpha}{(1+\alpha)^3} \ln[1 - (1+\alpha)x^*] . \quad (5.12)$$

Equation (5.12) leads to the asymptotic solution:

$$\lim_{t^* \rightarrow \infty} x^* = \frac{1}{1+\alpha} . \quad (5.13)$$

Therefore, the filling length x of the fluid cannot exceed $L/(1+\alpha)$. At this filling length, the force due to the pressure of trapped air volume F_p is equal to the surface force F_s .

Considering the dissolution of gas in liquid, the mass of trapped gas in the channel reduces gradually over time. Under a high Laplace pressure, the gas dissolves in liquid. The gas molecules in the liquid phase then diffuse out of the channel due to the concentration gradient. The dissolution of gas into liquid phase is governed by Henry's law while the diffusion is governed by Fick's law. With c the concentration of gas molecules at the meniscus and c_0 the concentration at the channel entrance, the Henry's law reads:

$$c = k_H p \quad (5.14)$$

$$c_0 = k_H p_0 . \quad (5.15)$$

The Fick's law gives the mass flux of the gas molecules in the channel:

$$\Phi_m = \frac{D_d M (c - c_0)}{x} \quad (5.16)$$

where D_d is the diffusion coefficient of the gas molecules in liquid and M is the molar mass of the gas. The ideal gas law applied to the trapped gas is:

$$p = \frac{\mathcal{R}T}{Mhw(L-x)}m \quad (5.17)$$

$$p_0 = \frac{\mathcal{R}T}{MhwL}m_0 \quad (5.18)$$

where m_0 is the initial mass of the gas. The force balance Eq. (5.1) has now the form:

$$2\sigma w \cos \theta = \frac{12\mu u}{h}wx + hw(p - p_0) . \quad (5.19)$$

From Eqs. (5.14), (5.15), (5.16), (5.17), (5.18) and (5.19), we obtain:

$$\left\{ \begin{array}{l} \frac{h}{12\mu x} \left[2\sigma \cos \theta - \frac{\mathcal{R}T}{Mw} \left(\frac{m}{L-x} - \frac{m_0}{L} \right) \right] = \frac{dx}{dt} \\ \frac{D_d \mathcal{R}T k_H}{x(L-x)L} [mL - m_0(L-x)] = -\frac{dm}{dt} . \end{array} \right. \quad (5.20a)$$

$$\quad (5.20b)$$

In addition to the dimensionless variables x^* , t^* , and α as in (5.8), (5.9) and (5.10), the dimensionless mass m^* and the parameter β are introduced:

$$m^* = \frac{m}{m_0} \quad (5.21)$$

$$\beta = \frac{6\mu D_d \mathcal{R}T k_H}{h\sigma \cos \theta} = \frac{\tau_{\text{capillary}}}{\tau_{\text{diffusion}}} \mathcal{R}T k_H . \quad (5.22)$$

Where the characteristic time for gas molecules to diffuse from one end to the other end of the nanochannel is $\tau_{\text{diffusion}} = L^2/(2D_d)$. The parameter $\mathcal{R}T k_H$ expresses the concentration ratio of gas molecules in gas phase and in the liquid. System of equations (5.20) then has the dimensionless form:

$$\begin{cases} \frac{1}{x^*} - \alpha \left(\frac{m^*}{1-x^*} - 1 \right) &= \frac{dx^*}{dt^*} \\ \beta \frac{1-m^*-x^*}{x^*(1-x^*)} &= \frac{dm^*}{dt^*} \end{cases} \quad (5.23a) \quad (5.23b)$$

System of equations (5.23) is difficult to solve analytically. However, it can be solved numerically. This numerical result and experimental results are compared later in Fig. 5.7.

The gas absorption theory shows a two-stage-filling pattern. The filling speed in the second stage can be estimated by:

$$u = \lim_{x^* \rightarrow 1} \frac{dx}{dt} = \lim_{x^* \rightarrow 1} \frac{2\tau_{\text{capillary}}}{L} \frac{dx^*}{dt^*} \quad (5.24)$$

Equation (5.23a) can be rewritten as:

$$\frac{\alpha x^{*2} + \alpha m^* x^* + (1-\alpha)x^* - 1}{x^{*2} - x^*} = \frac{dx^*}{dt^*} \quad (5.25)$$

Limitation of Eq. (5.25) when $m^* \rightarrow 0$ and $x^* \rightarrow 1$ has $\frac{0}{0}$ form. Therefore, l'Hôpital theorem is applied to find $\lim_{x^* \rightarrow 1} \frac{dx^*}{dm^*}$. For the case of small β , the dimensionless speed v^* is:

$$v^* = \lim_{x^* \rightarrow 1} \frac{dx^*}{dt^*} = \frac{\beta}{1+\alpha} \quad (5.26)$$

If β is considerable, the asymptotic value is:

$$v^* = \frac{1}{2} \left[1 + \alpha + \beta - \sqrt{4\alpha\beta + (-1 - \alpha + \beta)^2} \right] \quad (5.27)$$

Details of the derivation are presented in Appendix D. The filling speed is derived from Eq. (5.26) as:

$$\lim_{x \rightarrow L} \frac{dx}{dt} = \frac{D_d k_H \mathcal{R}T}{L \left(1 + \frac{hp_0}{2\sigma \cos \theta} \right)} \quad (5.28)$$

This result shows that the filling speed in this stage does not depend on the viscosity, but directly depends on the diffusivity and Henry coefficient. That means the filling in this stage solely depends on the gas absorption process. The relationship between dimensionless

speed and the dimensionless parameters α and β is described in Figs. 5.1 and 5.2. The dimensionless parameter α is directly proportional to the atmospheric pressure p_0 , while β is independent to p_0 . Therefore, the relationship of the dimensionless speed v^* to α also reflects the relationship of the dimensionless speed to p_0 . Figure 5.2 shows that increasing atmospheric pressure p_0 and α will reduce the filling speed, because higher p_0 means there are more gas molecules trapped in the channel. A longer time would be needed to diffuse the gas out.

The exact time needed to completely fill the channel is difficult to determine, because it requires the exact solution of Eq. (5.23). However, the second stage of filling normally takes much longer than the first stage to complete. Therefore, this stage can be used to estimate the total filling time. The filling length of the second stage can be determined by unfilled length as in Eq. (5.13):

$$\Delta x^* = 1 - \lim_{t^* \rightarrow \infty} x^* = \frac{\alpha}{1 + \alpha} . \quad (5.29)$$

Dividing Eq. (5.29) by Eq. (5.26) gives:

$$\Delta t^* = \frac{\Delta x^*}{v^*} = \frac{\alpha}{1 + \alpha} \frac{1 + \alpha}{\beta} = \frac{\alpha}{\beta} = \frac{h^2 p_0}{12 \mathcal{R} T \mu D_d k_H} . \quad (5.30)$$

The absolute filling time in the second stage is then given by:

$$\Delta t = \Delta t^* \frac{6 \mu L^2}{h \sigma \cos \theta} = \frac{h p_0 L^2}{2 \sigma \cos \theta \mathcal{R} T D_d k_H} . \quad (5.31)$$

Equation (5.31) shows that the total filling time is approximately proportional to the channel height h . Figure 5.3 shows the filling time of the second stage with various parameters. The filling process takes seconds to minutes in nanochannels but may take days or even years in micro- or minichannels. Moreover, within a meaningful aspect ratio, micro- and minichannels are longer than nanochannels. Because the filling time is proportional to square of the channel length, the filling time in such long channels is even longer. This explains why in a bigger channel the liquid practically does not fill until the end. With the assumption that the filling time of the second stage dominates that of the first stage, Eq (5.31) shows that the total filling time is proportional to the atmospheric pressure p_0 .

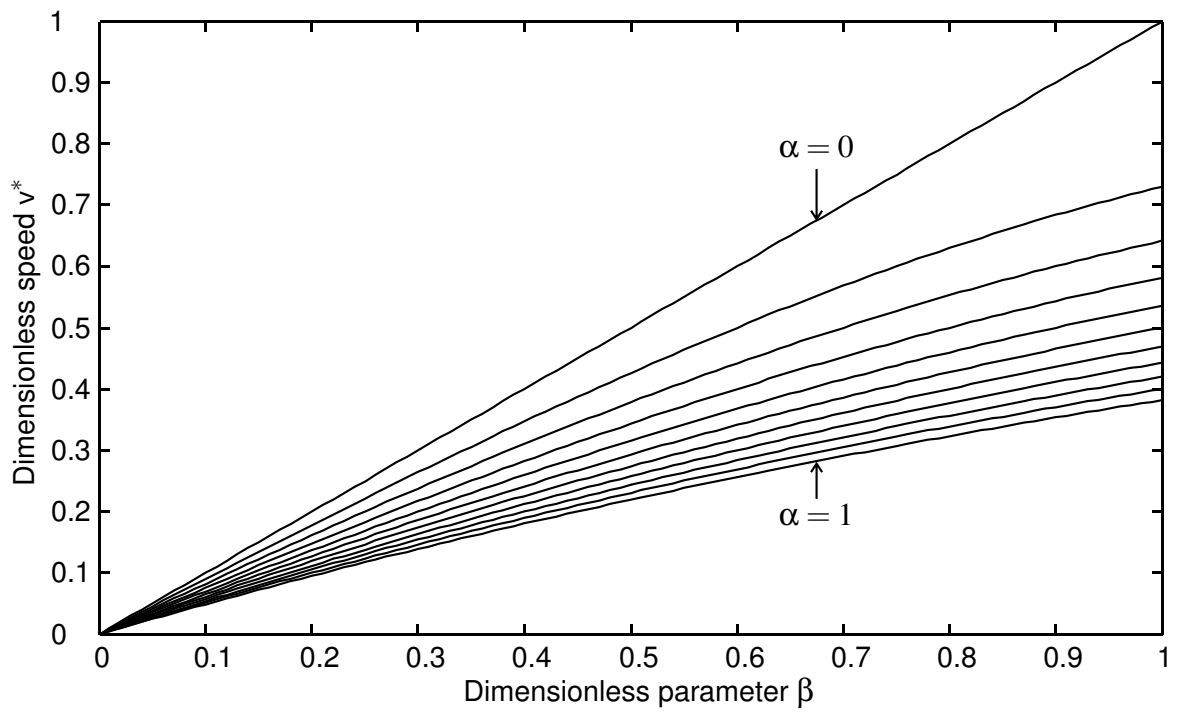


Figure 5.1: Dimensionless speed with different values of α

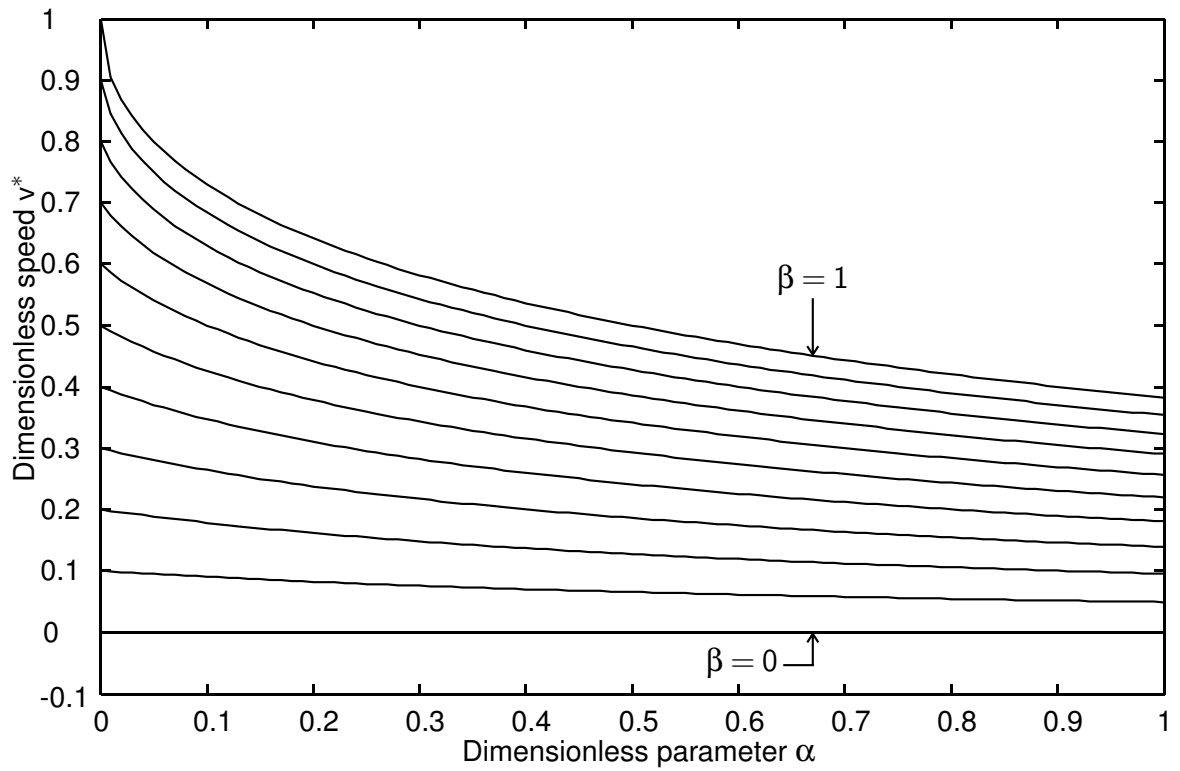


Figure 5.2: Dimensionless speed with different values of β

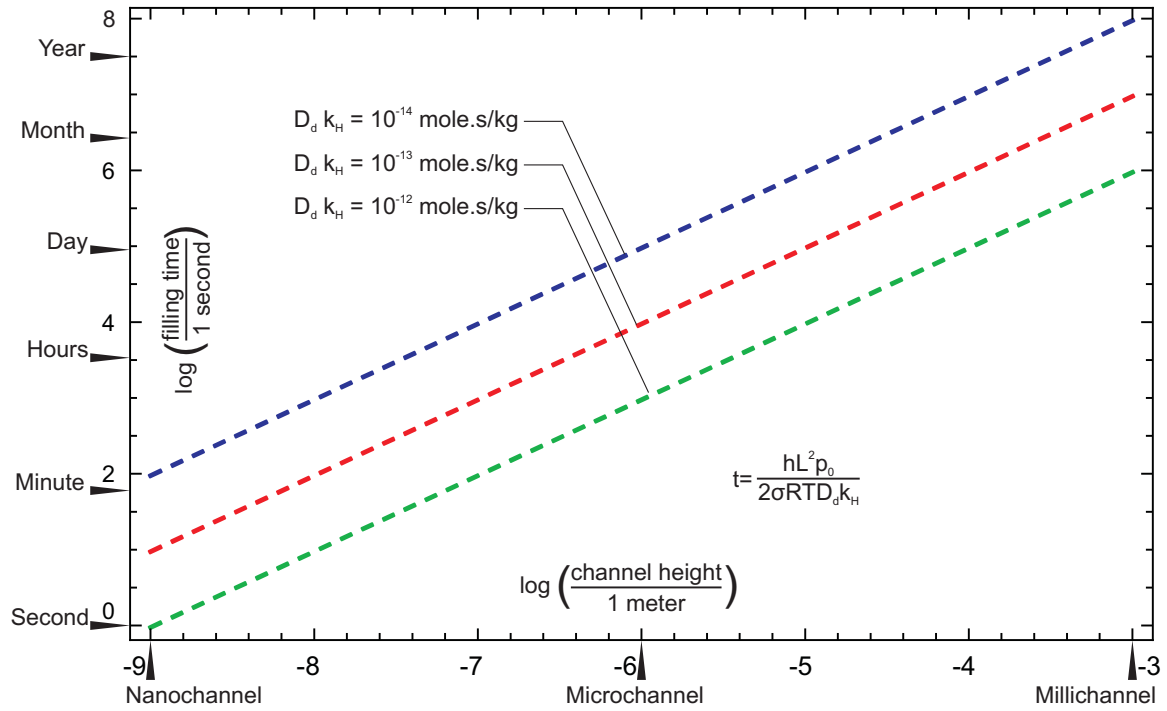


Figure 5.3: Approximated filling time with different parameters

5.3 Experiments

5.3.1 Equipments and Materials

The experiments were performed in nanochannels of 10 μm width and 45 nm depth. The lengths of the nanochannels range from 10 μm to 8 mm (10 μm , 50 μm , 100 μm , 300 μm , 500 μm , 1 mm, 1.5 mm, 2 mm, 2.5 mm, 3 mm, 3.5 mm, 4 mm, 5 mm, 6 mm, 7 mm, 8 mm). The channels were fabricated by reactive ion etching (RIE) process on a silicon wafer. A glass plate was bonded on top of the silicon wafer by anodic bonding to seal the nanochannels. The entrances of the nanochannels are connected to a microchannel. Two ends of the microchannel are accessible through reservoirs etched through the silicon wafer as described earlier in Chapter 3. Figure 5.4 shows the schematic of the chip with nanochannels. During the experiments, the silicon chip was observed with the inverted microscope (Zeiss Observer D1) with the reservoirs facing up. The fluid was introduced into one of the reservoirs and started to fill in the microchannel and nanochannels by capillary force. Deionized water (DIW), ethanol, and isopropanol were used as the filling fluids.

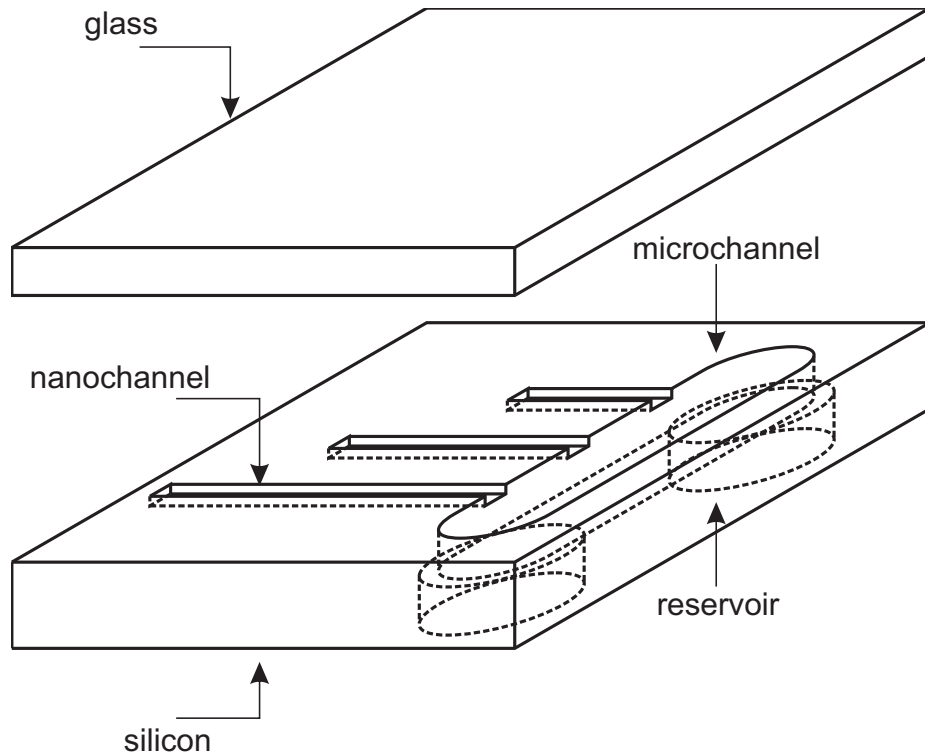


Figure 5.4: A silicon chip with nanochannels used in capillary filling experiment in closed-end nanochannels.

To keep ethanol and isopropanol from wetting the outer surface of the chip, a spacer made from polydimethyl siloxane (PDMS) was placed above the reservoirs. The temperature and relative humidity were measured before each experiment. The images observed during the experiment through the microscope were recorded by a CCD camera (EMCCD AndorIQ). The images were saved as 16-bit gray-scale multi-images uncompressed TIF file with size of 1004 pixel x 1002 pixel. The captured time was saved in a separated text file.

5.3.2 Methods

To investigate the interaction among the liquid, solid and air in closed-end nanochannels qualitatively and quantitatively, the filling processes were observed with different magnifications and time scales. The experiments were carried out in the following steps:

Step 1 recorded the filling process from the entrance of the nanochannels until the end of the 3-mm-long nanochannels. Objective lens magnification of $2.5\times$ and camera magnification $1\times$ were used. The field of view was approximately $3\text{ mm}\times 3\text{ mm}$. The exposure time was set at 10 ms. The movie was recorded with highest frame rate available

(approximately 17 fps).

Step 2 recorded the development of the meniscus during the filling process. One of the closed ends of the nanochannels was chosen for the observation. Objective lens magnification of $20\times$ and camera magnification of $1\times$ were used. Video setting was the same as in step 1.

Step 3 checked whether the liquid can fill until the end of the nanochannels after a long filling time. The still images of the closed ends were recorded with objective lens magnification of $20\times$ and camera magnification $1\times$.

5.4 Results and Discussions

Figure 5.5 plots the square of filling length versus filling time of ethanol and isopropanol in nanochannels with different length. The method used for extracting the filling length from video files is the same as described in Section 4.3. The linear characteristic of the graph in the first filling stage suggests that the filling process follows Washburn's law:

$$x = \sqrt{at} \quad (5.32)$$

where a is the Washburn coefficient. In a slit-shape channel, $a = (\sigma \cos \theta h) / (3\mu)$. In Fig. 5.5, the slopes of the data lines in the neighbourhood of the axes origin were used to calculate the experimental Washburn coefficients. The data of the longest channel (2.5 mm) in each case was used for numerical fitting because this channel length provides the most data points. Washburn coefficient depends on the surface tension, the contact angle and the viscosity of the filling fluid. It is convenient to express the change in Washburn coefficient using the effective viscosity and to consider the surface tension and the contact angle are the same as their bulk values. Using the experimental Washburn coefficient, the effective viscosities of ethanol and isopropanol are taken as 177% and 195% of their respective bulk values at 25°C.

In the model presented in Section 5.2, we adopt the isothermal hypothesis, which means the temperature of the system is stable and always equal to the environmental temperature. This assumption requires perfect heat dissipation. In practice, when the liquid advances in the nanochannel, the trapped air is compressed and the temperature increases. The temper-

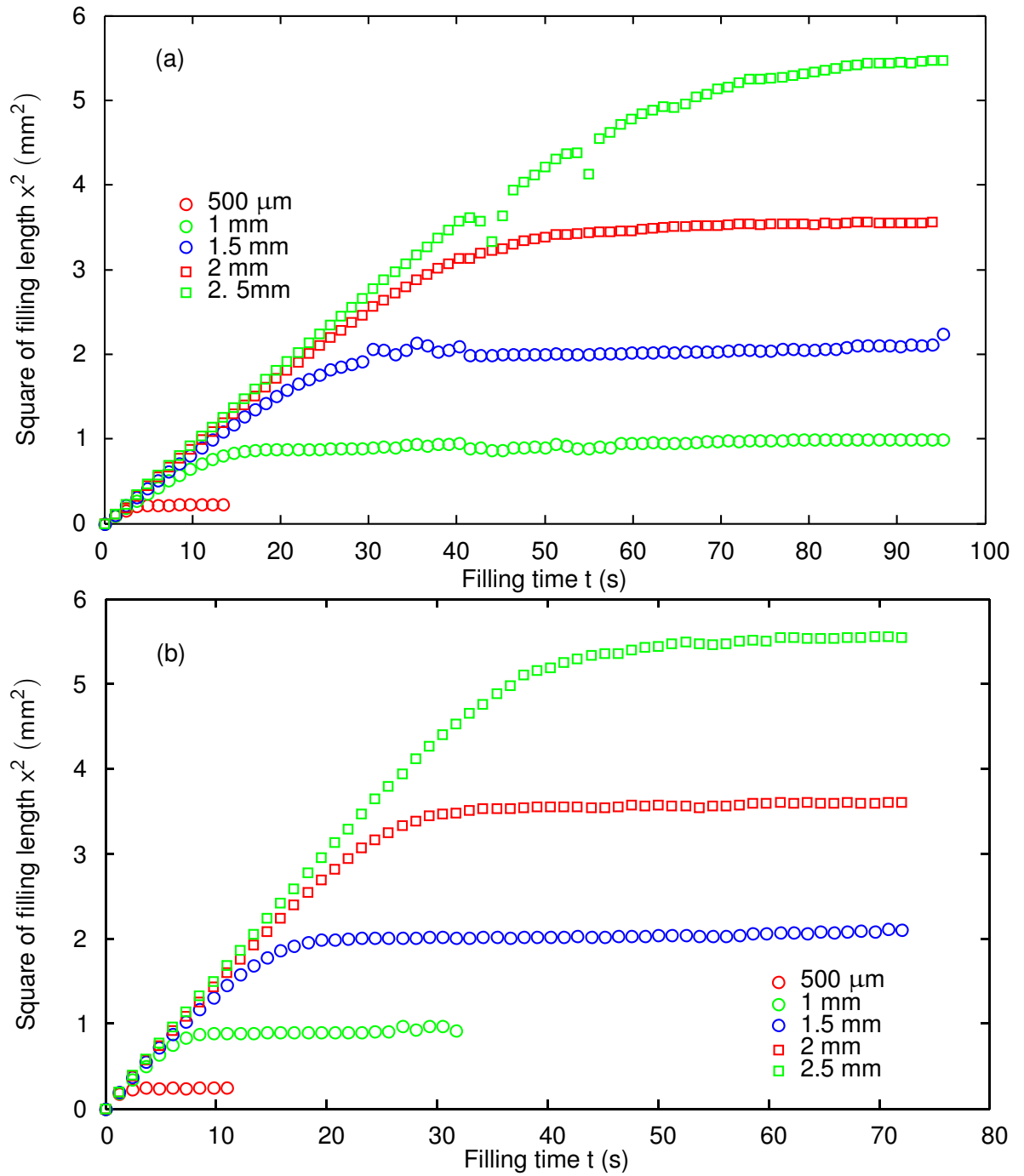


Figure 5.5: Square of filling length versus time in closed-end nanochannels with different lengths L (a) Isopropanol ; (b) Ethanol.

ature of the compressed air is higher than that of the environment because of the finite heat transfer coefficient of the material. The pressure of the compressed air is therefore also higher than the value in our hypothesis. This additional pressure increase further slows down the filling speed. For example, isopropanol fills a 45-nm-height nanochannel leads to $\alpha \approx 0.1$, with α the ratio between the atmospheric pressure and the Laplace pressure, as defined in Eq. (5.10). Compression ratio CR of the air is defined as the ratio between initial air volume and final air volume. With the isothermal assumption, the final pressure of the air should equal to the Laplace pressure:

$$\text{CR} = \frac{L}{L-x} = \frac{1}{1-x^*} . \quad (5.33)$$

With Eq. (5.13), the compression ratio CR approaches $(1 + \alpha)/\alpha \approx 10$, which means x approaches 0.9 L. The isentropic (no heat dissipating) assumption and a heat capacity ratio $\gamma \approx 1.4$ result in:

$$\begin{aligned} \frac{1}{\alpha} &= \frac{p_{\text{Laplace}}}{p_0} = \left(\frac{L}{L-x}\right)^\gamma = \left(\frac{1}{1-x^*}\right)^\gamma \approx 10 \\ &\quad \frac{1}{1-x^*} \approx 5 \\ \Rightarrow x^* &= \frac{x}{L} \rightarrow 0.8 . \end{aligned} \quad (5.34)$$

The limit of filling length with isentropic assumption is lower than that with isothermal assumption. This suggests that lower heat dissipation may cause the reduction in filling speed, or an increase in effective viscosity. The phenomenon mainly affects the first stage of filling, where a high compression ratio is reached in a short period of time, hence heat dissipation is still low. However, analysing the heat transfer process is complicated and beyond the scope of this work. Therefore, we used numerical fitting data for the effective viscosity, although its value seems to be higher than those reported previously for the case of open nanochannel [35, 36, 42, 55].

A similar experiment was also performed using water as filling liquid. Qualitatively, the result shows similar trend as those with ethanol and isopropanol. However, the chaotic region of the meniscus during the second stage of filling is significantly larger, resulting in a large amount of noise, as shown in Fig. 5.6. The experiment process using water is beyond our capability of image processing and data analysis. Therefore, this work does not compare theory with experiment for the case of water.

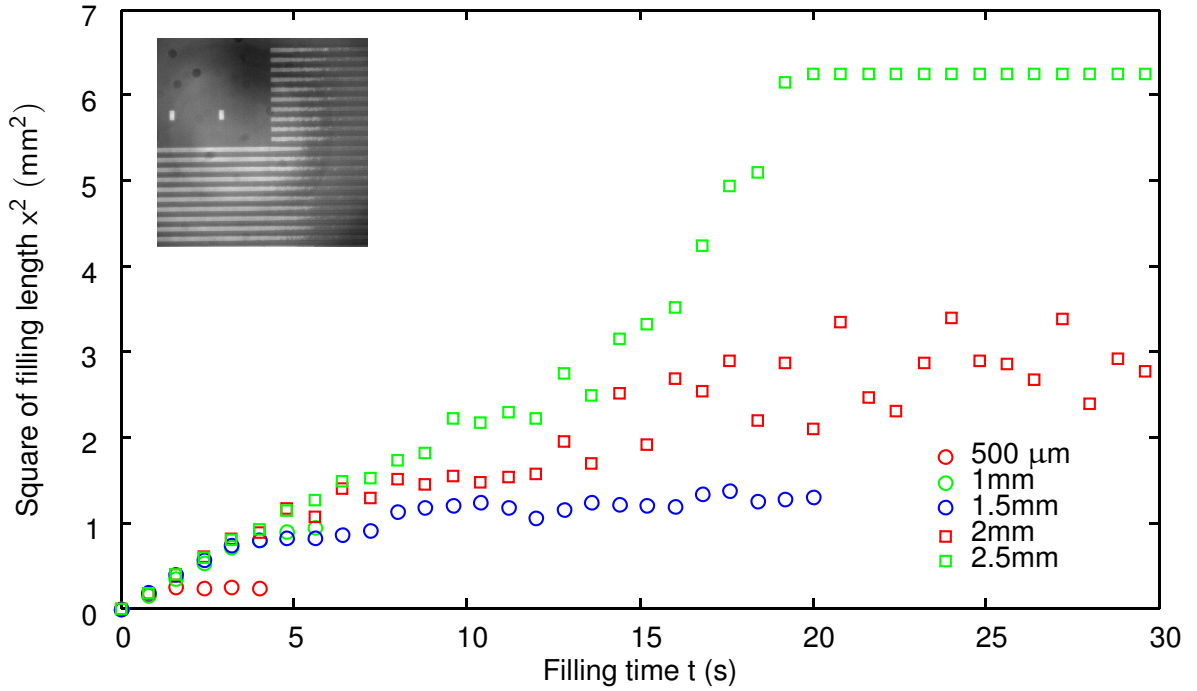


Figure 5.6: Square of filling length versus time of deionized water in closed-end nanochannels with different lengths L . The inset shows the end of 0.5 mm channels, with a large region of irregular meniscus, the main cause of noise in data analysis

Figure 5.7 presents the normalized filling length as a function of normalized time of the capillary filling process in closed-end nanochannels. Air is a mixture of oxygen, nitrogen and a minor amount of other gases. Due to the different Henry coefficients and diffusion coefficients of the components of the air, a theory for absorption of air is more complex than that of a single gas as modelled by Eqs. (5.23a) and (5.23b). In this work, we introduce effective values of air to serve the single-gas model. Few works in the past provided values of the Henry coefficient k_H and the diffusion coefficient D_d . Schnabel et al. used simulation to predict the Henry coefficient of various gases in ethanol, including oxygen and nitrogen [111]. The simulation results were compared to previous experimental data. From this work, the Henry coefficient of oxygen in ethanol at 300K is approximately $9.5 \times 10^{-3} \text{ mole}/(\text{bar} \cdot \text{liter})$ and that of nitrogen in ethanol is approximately $6.1 \times 10^{-3} \text{ mole}/(\text{bar} \cdot \text{liter})$. Ferrell and Himmelblau [112] performed an experimental investigation on the diffusion coefficients of oxygen and nitrogen in water, which are $2.2 \times 10^{-9} \text{ m}^2/\text{s}$ and $2.0 \times 10^{-9} \text{ m}^2/\text{s}$ at 25°C respectively. These values are good approximations for the respective diffusion coefficients in ethanol and isopropanol. Accord-

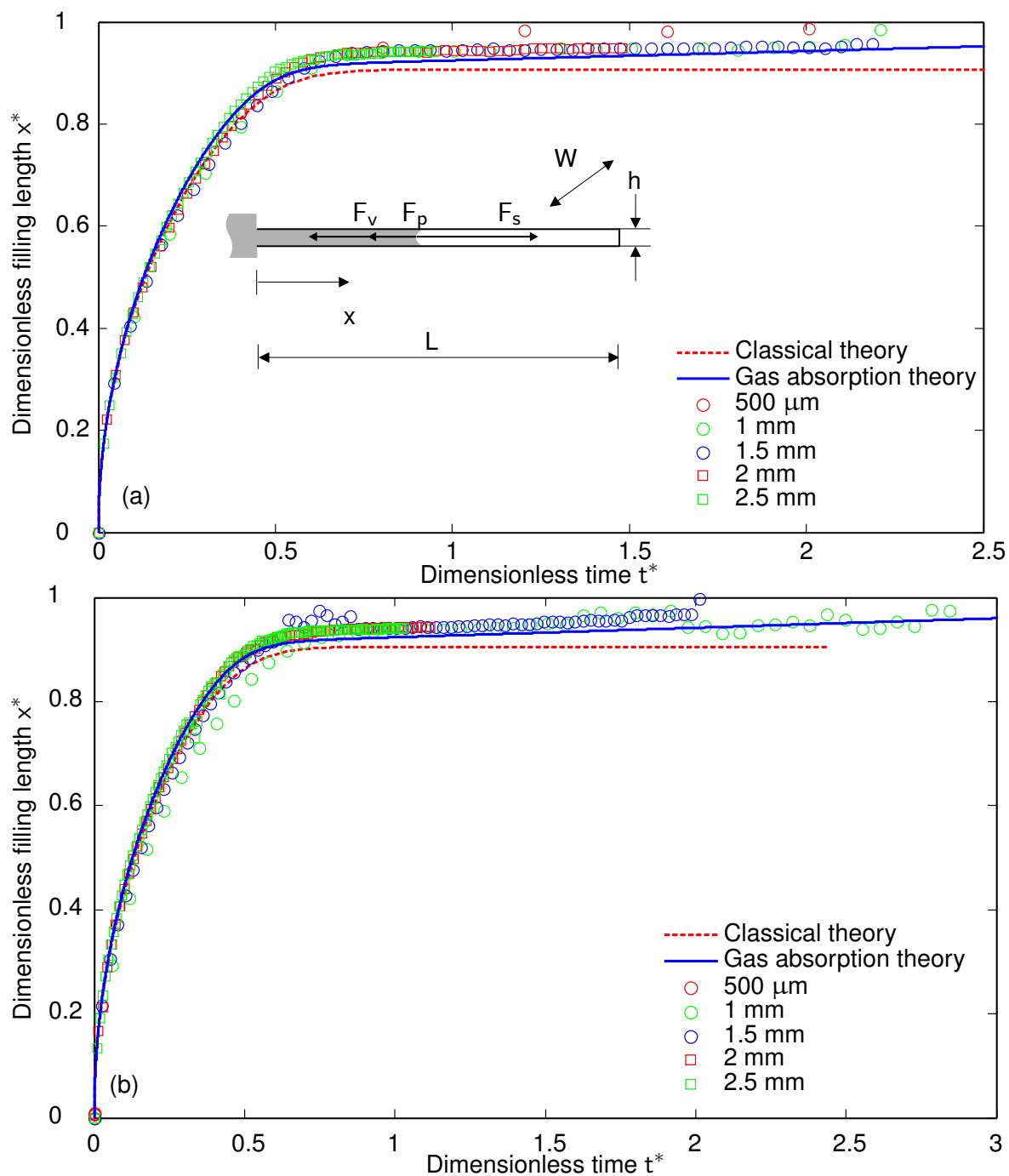
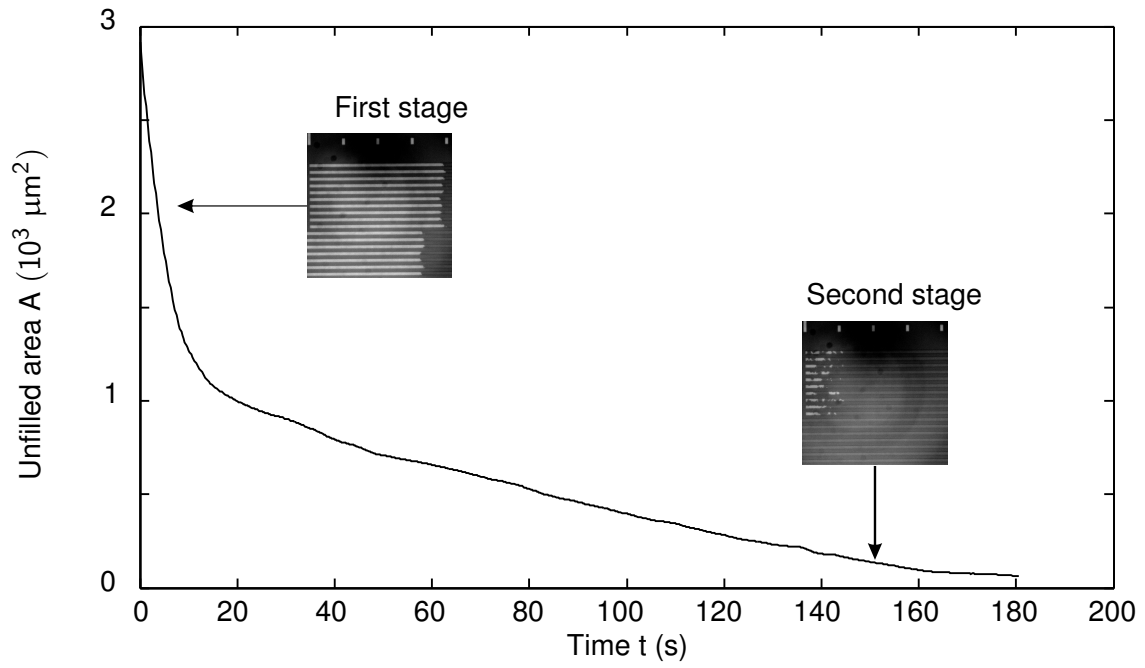


Figure 5.7: Normalized filling length versus normalized time in closed-end nanochannels with different lengths L (solid line: model with gas absorption, dashed line: model without gas absorption, circles and squares: experimental data): (a) Isopropanol (effective viscosity is 177% of the bulk value); (b) Ethanol (effective viscosity is 195% of the bulk value).

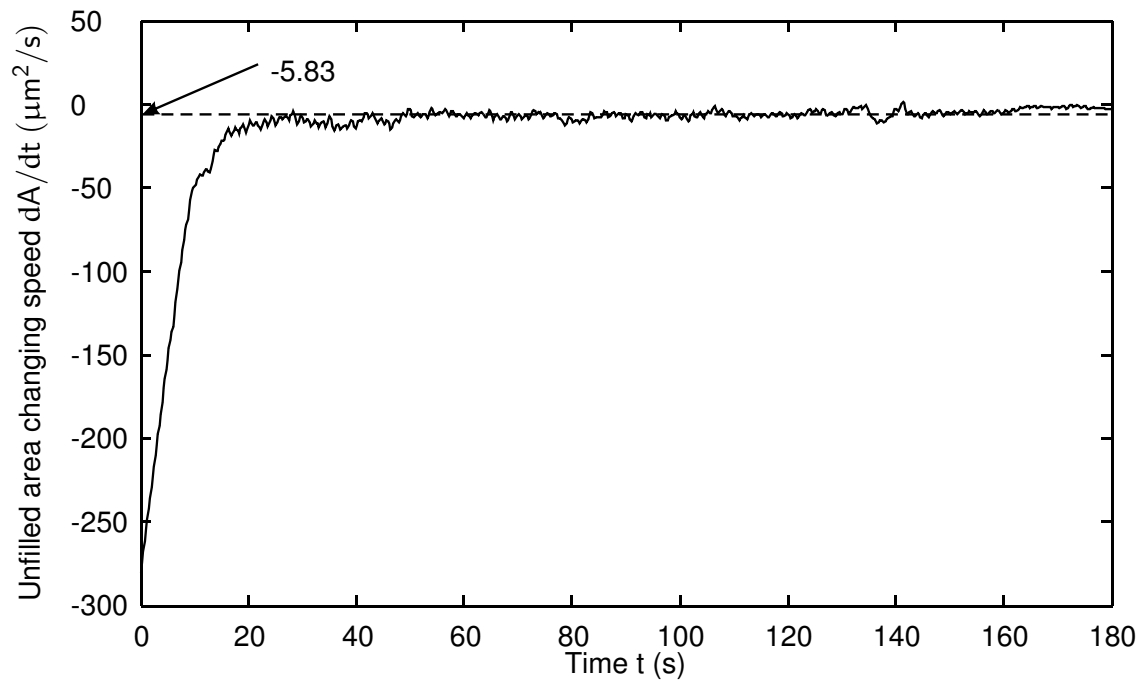
ing to the above results, the effective values of $k_H D_d$ in the case of air dissolve in ethanol and isopropanol are estimated to be on the order of 10^{-13} to 10^{-12} mole $\cdot$ s/kg. In Fig. 5.7, values of $k_H D_d = 6.5 \times 10^{-13}$ mole $\cdot$ s/kg for ethanol and 3.5×10^{-13} mole $\cdot$ s/kg for isopropanol give good fitting to experimental data. The experimental filling process consists of two stages. In the first stage, the force of the pressurized air F_p was negligible, the filling process resembled that of capillary filling in open-end nanochannels. In the second stage, the trapped air was compressed under the effect of the surface force. The force F_p was comparable to the surface force F_s . Under the high pressure, the absorption of air became more significant. The meniscus still slowly advanced toward the end of the channel and finally filled the channel completely. This experimental observation agrees well with the model with gas absorption.

In the final filling stage, the shape of the meniscus was irregular. The chaotic movement of the meniscus created a region where liquid and gas coexist, as shown in the insets of Figs. 5.6 and 5.8. This region defines the error in determination of the horizontal coordinate of the meniscus. Examples of such errors are chaotic data shown in Fig. 5.6 or in the data of the 0.5-mm-long channel, second filling stage, Fig. 5.8(a). Therefore, to analyse this second stage, the remaining unfilled area of the nanochannels was measured. Images at the end of the nanochannels with a higher magnification were used for the analysis. Figure 5.8(a) presents the amount of unfilled area at the end of the filling process of ethanol in a 2-mm-long nanochannel with respect to time. In Fig. 5.8(a), the amount of unfilled area reduces linearly with time. This linear behaviour is confirmed in Fig. 5.8(b), which shows the changing rate of unfilled area as a function of time. Experimental results showed that during the first stage of the filling process, the meniscus of the liquid advanced faster and the shape of the meniscus was well defined. In the second stage, when the meniscus approached the closed end, the filling speed was much slower and the shape of the meniscus became irregular. Two stages of filling were distinguished clearly in both cases of ethanol and isopropanol. During the second stage of filling, air bubbles were captured by irregular movement of the meniscus. The captured bubbles shrink and gradually disappear. This phenomenon can be considered as the dissolution process of air into the liquid under the high Laplace pressure.

Figure 5.10 illustrates the capillary filling processes in open-end nanochannels with



(a)



(b)

Figure 5.8: Unfilled area (a) and its changing rate (b) versus time at the end of filling process of ethanol in a 2-mm-long nanochannel.

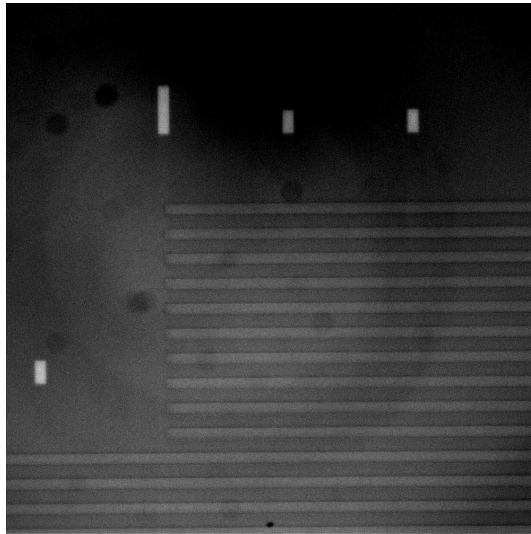


Figure 5.9: Ethanol completely fills the nanochannels of 2.5 mm length

and without electroviscous effect, closed-end nanochannel with and without consideration of gas absorption. The filling process without gas absorption is suitable for filling in microchannels or larger channels, as the compression pressure of the trapped gas is small in those cases. The filling process with gas should be applied for filling in nanochannels. At the first stage of the filling process, the surface tension dominates. The contribution of gas compression is small. There is little difference among three filling modes (a). When the filling length is large enough, the pressure due to the compression of trapped gas causes a reduction in filling speed in closed end (b). Without gas absorption, the liquid in closed-end channels reaches its limited length and stops filling (c) while the air absorption cause the liquid to completely fill the channel (d).

In conclusion, this chapter investigates the air absorption in liquid by performing capillary filling in closed-end nanochannels. The liquid in closed-end silicon nanochannels did not stop at the filling length predicted by the classical theory but completely filled the channels. A mathematical model was built with consideration of the trapped air absorption into the filling liquid. This model explained well the filling behaviour of the fluid in nanochannels. The results show that gas absorption in liquid is important in nanoscale that should be considered while investigating other transport phenomena of fluids in nanochannels.

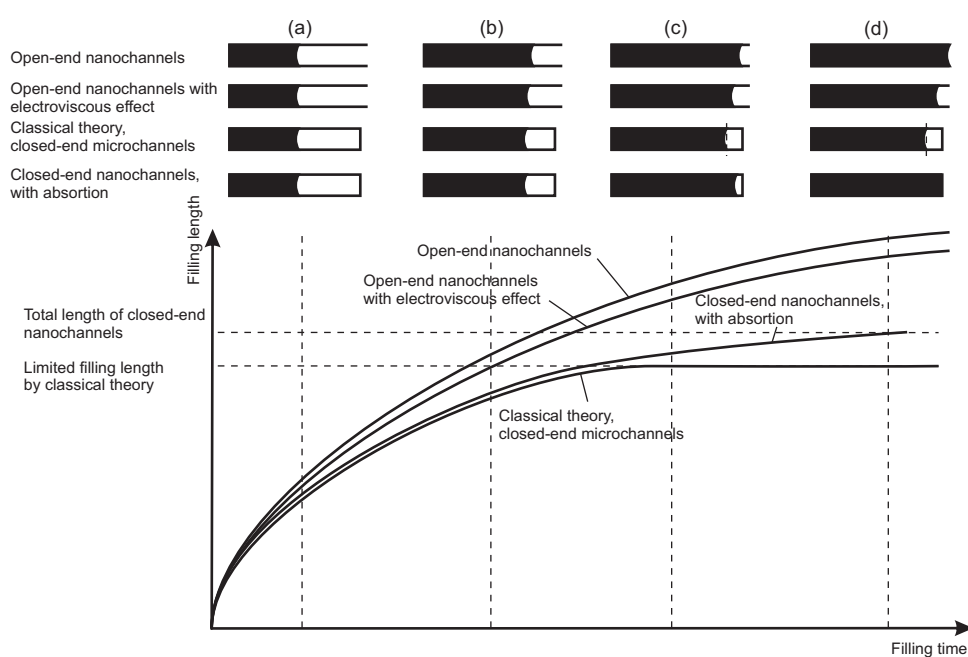


Figure 5.10: Illustration of capillary filling processes in open-end nanochannels, closed-end nanochannel with and without consideration of gas absorption. The filling patterns are similar at the early stage (a) for all three filling modes. The compression of gas then causes a reduction in filling speed in closed-end channels (b). Without gas absorption, the liquid stops filling at a limited length (a). With gas absorption, the liquid can completely fill the channels (d).

Chapter 6

Evaporation and Condensation in Nanochannels

6.1 Background

The experimental observations in Chapter 4 and Chapter 5 show the formation of air bubbles in the filling liquid. The surface energy of the bubbles is converted from the kinetic energy of the filling. Consequently, the formation of air bubbles reduces the capillary filling speed. This phenomenon depends on complicated physics. There is no complete investigation on the formation of air bubbles. Such a complete investigation is not in the scope of this thesis. However, the observations related to the formation of air bubbles are useful for future works. This chapter presents the investigation of evaporation and condensation in nanochannels. The theories on evaporation and condensation are reviewed in the context of nanochannels, especially considering the unique characteristic of the nanoscale. Qualitative comparisons between theoretical and experimental data are made to evaluate the theories, and also to point out the direction for future works to approach the complete understanding on the formation of air bubbles.

Each section in this chapter consists of a theoretical model in the first sub-section. The Results and Discussions sub-section of each section describes the experiment which was designed to observe the corresponding phenomenon. The Results and Discussions sub-section also compares the experimental data to the theoretical model. Most comparisons are

done with a fitting factor; therefore, the comparisons are more qualitative than quantitative.

6.2 Evaporation in Nanochannels

6.2.1 Theoretical Analysis

Fickian Diffusion

Fickian diffusion is due to viscous movement of molecules in a surrounding medium. The formula for Fickian diffusion (including diffusion of Brownian particles) is

$$\frac{p(x) - p(x + \Delta x)}{\Delta x} = \frac{F(x) - F(x + \Delta x)}{\mathcal{A}\Delta x} = \frac{NF_p}{\mathcal{A}\Delta x} \quad (6.1)$$

where p is the pressure, F is the force acting on the particles, F_p is the average force acting on each particle and N is the total number of particles. Let $c = N/(\mathcal{A}\Delta x)$ be the concentration of the particles, the formula becomes

$$\frac{\partial p}{\partial x} = cF_p. \quad (6.2)$$

Viscous motion of each particle with velocity u is given by:

$$F_p = m\upsilon u \quad (6.3)$$

where m is the mass of each particle and υ is the friction coefficient of the fluid.

Assuming that the particles follow the equation of state of the ideal gas, the pressure is determined as:

$$p = \frac{nN_A}{\Delta V} \frac{\mathcal{R}}{N_A} T = ckT \quad (6.4)$$

where N_A is the Avogadro's number and $\mathcal{R}$ is the universal gas constant. Taking partial derivative of (6.4) with respect to x results in:

$$\frac{\partial p}{\partial x} = kT \frac{\partial c}{\partial x} = -cF_p = -cm\upsilon u. \quad (6.5)$$

The definition of diffusivity leads to:

$$cu = \frac{N}{\mathcal{A}\Delta x} \frac{\Delta x}{\Delta t} = \frac{N}{\mathcal{A}\Delta t} = -D_F \frac{\partial c}{\partial x}. \quad (6.6)$$

From (6.5) and (6.6), the diffusion coefficient is:

$$D_F = \frac{kT}{m\bar{v}} . \quad (6.7)$$

For spherical particles with radius r and viscosity μ , Eq. (6.7) becomes:

$$D_F = \frac{kT}{6\pi r\mu} . \quad (6.8)$$

Knudsen Diffusion

Knudsen diffusion is caused by thermal motion of the particle. Knudsen diffusion does not depend on other particles and the viscosity because the characteristic length is lower than the mean free path of the particles. The Knudsen diffusivity is assumed to be the same as the tracer diffusivity. Concentration distribution function of diffusion in a 3D-space with Knudsen diffusivity D_K and initial condition of $c(r, t)|_{t=0} = c_0\delta(r)$ is:

$$c(r, t) = c_0 \frac{1}{(4\pi D_K t)^{3/2}} \exp\left(-\frac{r^2}{4D_K t}\right) . \quad (6.9)$$

The mean-square of the position r is given by:

$$\langle r^2 \rangle = \frac{1}{c_0} \int_0^\infty \frac{1}{(4\pi D_K t)^{3/2}} \exp\left(-\frac{r^2}{4D_K t}\right) 4\pi r^2 r^2 dr = 6D_K t . \quad (6.10)$$

Therefore, the self-diffusion coefficient is determined by Einstein relation:

$$D_K = \lim_{t \rightarrow \infty} \frac{1}{6N} \frac{|r - r_0|^2}{t} . \quad (6.11)$$

Diffusion Theory

The diffusion theory assumes that the transport of fluid in a nanochannel is governed only by the diffusion process. The drying speed is determined by the diffusion flux of the vapour molecules only. The diffusion flux (mole per unit area per unit time) is:

$$\Phi = D_d \frac{dc}{dx} \quad (6.12)$$

where Φ is the mass flux and c is the molar concentration of the fluid vapour and D_d is the diffusion coefficient of the vapour. Using ideal gas assumption, the concentration is:

$$c = \frac{P}{\mathcal{R}T} . \quad (6.13)$$

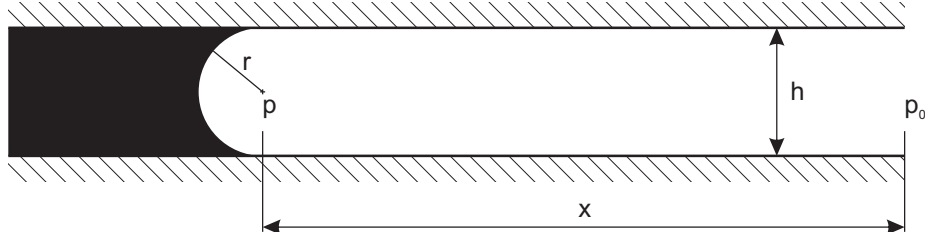


Figure 6.1: Model of drying process by diffusion.

Because the flux is constant along the nanochannel, the concentration gradient is:

$$\frac{dc}{dx} = \frac{\Delta c}{x} = \frac{p - p_0}{\mathcal{R}Tx} \quad (6.14)$$

where p_0 is the vapour pressure at the exit of the channel. From (6.12) and (6.13), the drying speed is derived as:

$$u_{\text{dry}} = \Phi V_M = D_d V_M \frac{p - p_0}{\mathcal{R}Tx} \quad (6.15)$$

where V_M is the molar volume of the liquid. The saturation vapour pressure at the meniscus is calculated by Kelvin equation:

$$\mathcal{R}T \ln \frac{p}{p_{\text{sat}}} = V_M \sigma \left(\frac{1}{r_1} + \frac{1}{r_2} \right) \quad (6.16)$$

where p_{sat} is the saturation vapour pressure of liquid, σ is the surface tension, r_1 and r_2 are two perpendicular radii of curvature. In a totally wet slit-shape nanochannel, $r_2 \gg r_1 = -h/2$, Eq. (6.16) becomes:

$$\mathcal{R}T \ln \frac{p}{p_{\text{sat}}} = \frac{2V_M \sigma}{h} \Rightarrow p = p_{\text{sat}} \exp \left(-\frac{2V_M \sigma}{\mathcal{R}Th} \right). \quad (6.17)$$

Equation (6.15) becomes:

$$u_{\text{dry}} = \frac{dx}{dt} = D_d V_M \frac{p}{\mathcal{R}Tx} = D_d V_M \frac{p_{\text{sat}} \exp \left(-\frac{2V_M \sigma}{\mathcal{R}Th} \right) - p_0}{\mathcal{R}Tx} \quad (6.18)$$

with initial condition $x = 0$ at $t = 0$, the solution of Eq. (6.18) is:

$$x = \left[2D_d V_M \frac{p_{\text{sat}} \exp \left(-\frac{2V_M \sigma}{\mathcal{R}Th} \right) - p_0}{\mathcal{R}T} t \right]^{1/2}. \quad (6.19)$$

Knudsen Diffusion Regime

In a slit-shaped nanochannel, the characteristic length of the channel, e.g. the channel height, is smaller than the mean-free-path of the vapour molecules. Collisions between the particles and the channel walls happen more frequently than inter-particle collisions. The diffusion phenomenon is then said to be in Knudsen regime, rather than in Fickian regime. The Knudsen number (Kn) is used to determine whether the diffusion is in Knudsen regime or Fickian regime. The Knudsen number for a slit-shaped nanochannel is defined as:

$$Kn = \frac{\lambda_m}{h} \quad (6.20)$$

where λ_m is the mean-free-path of the molecules, with ideal gas approximation

$$\lambda_m = \frac{kT}{\sqrt{2}\pi d^2 p} \quad (6.21)$$

where d is the diameter of the molecules. For an air-vapour mixture in a nanochannel, the concentration of vapour is a function of time and position, therefore, the average diameter of particles is also a function of time. However, it is possible to estimate using the size of an ethanol molecule $d = 2 \times 1.96 \times 10^{-10}$ m [113]. Substituting $p \approx 1$ bar, $T \approx 298$ K and $h=45$ nm into Eq. (6.20) and Eq. (6.21) gives:

$$Kn \approx 1.34 . \quad (6.22)$$

This value of Knudsen number suggests the use of Knudsen diffusion regime [114].

In the literature, Knudsen diffusion in parallel pore model has been used to evaluate the mass transport in porous material [115, 116]. The Knudsen diffusion coefficient in straight cylindrical channel is evaluated by balancing the shear stress on the wall of the channel due to partially directional bombardment of particles and the pressure gradient [117]. Using the same approach, the diffusion coefficient in a slit-shaped nanochannel is:

$$D_K = \frac{2}{3} \sqrt{\frac{8kT}{\pi m}} h . \quad (6.23)$$

6.2.2 Experiments

The experimental setup to record the drying process of liquid in nanochannels is similar to that described in Section 5.3. After filling the nanochannels with liquids, compressed

Table 6.1: Parameters of ethanol

Parameters	Symbols	Values	Units
Fickian diffusion coefficient	D_F	1.19×10^{-5}	m^2/s
Knudsen diffusion coefficient	D_K	1.11×10^{-5}	m^2/s
Molar volume	V_M	5.83×10^{-5}	m^3/mole
Saturated vapour pressure	p_{sat}	7.87×10^3	Pa
Surface tension	σ	2.24×10^{-2}	N/m

Table 6.2: Parameters used in drying experiment

Parameters	Symbols	Values	Units
Channel height	h	45×10^{-9}	m
Molar gas constant	$\mathcal{R}$	8.31	$\text{Pa} \cdot \text{m}^3/\text{K} \cdot \text{mole}$
Room temperature	T	298	K

nitrogen was used to blow the liquid out of the microchannel. The drying process was recorded with an objective lens magnification of $2.5\times$ and camera magnification $1\times$. The exposure time was 10 ms. The interval between each frame was set to 200 ms (equivalent to 5 fps). The exact capturing time of each image was recorded automatically.

6.2.3 Results and Discussions

Figure 6.2 presents the square of drying length versus drying time. The figure shows a highly linear relationship between the square of the drying length and the drying time. The theoretical results are generated using Eq. (6.19) with the parameters given in Tab. 6.1 and Tab. 6.2, the data are taken from [105, 107, 108, 118]. The theoretical lines are plotted with different values of the exit vapour pressure p_0 . The diffusion is assumed to be in Knudsen regime. The experimental results show that fully filled channels dry faster than partially filled channels.

Unlike the results from previous experiment of other authors [119, 120], which suggest an increase in drying speed due to the effect of film flow and corner flow, this results showed a lower drying speed than expected by the theory, if the exit vapour pressure p_0 is assumed to be zero. The results can be explained by a reduction of saturated vapour pressure or diffusion coefficient. Figure 6.3 shows the theoretical lines with $p_0 = 0$ and different values of saturated vapour pressure p_{sat} . Lastly, with $p_0 = 0$ and $p_{\text{sat}} = 7.87 \text{ kPa}$, the average measured diffusion coefficient in a fully filled channel is at 63% of the theoretical value of

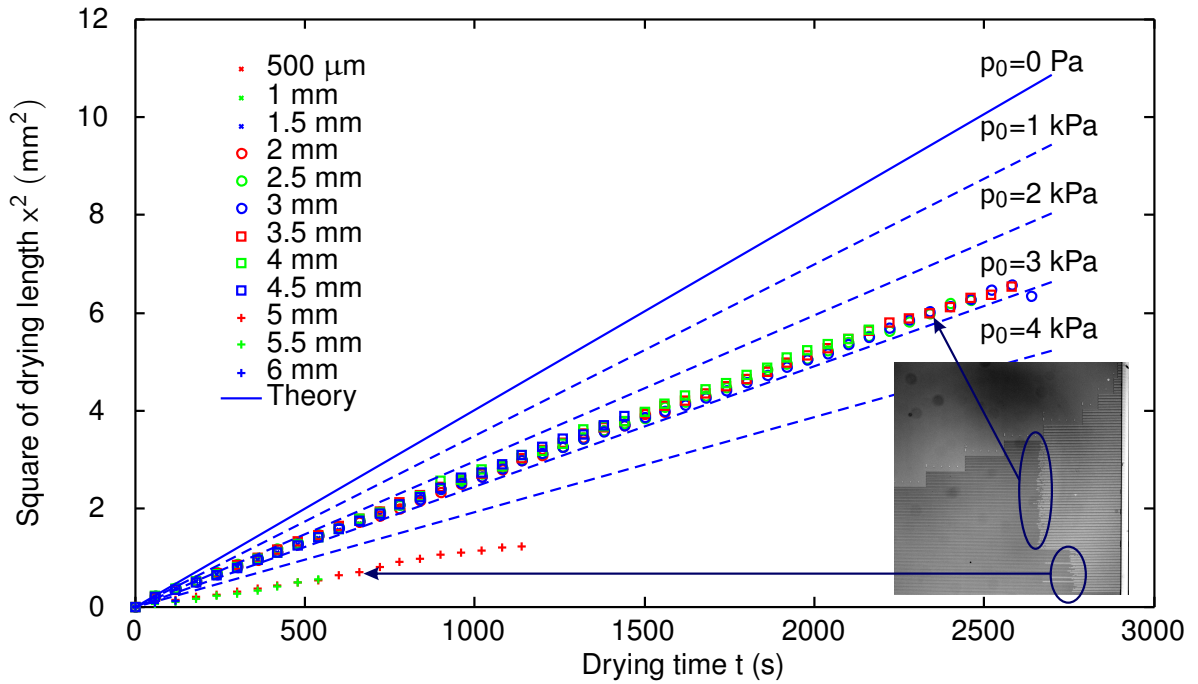


Figure 6.2: Square of measured drying lengths and theoretical prediction with different values of the exit vapour pressure p_0 ($p_{\text{sat}} = 7.87$ kPa).

D_K , Tab. 6.1. This result gives an actual picture of the parallel pore model which is usually used in literature to model the mass transport in porous material [115, 116].

In the parallel pore model, the porous material is represented by a matrix of parallel straight pores with a uniform cross-section. The phenomena such as capillary filling, evaporation, and condensation are described in this matrix by mathematical models. Due to the simple geometry, the mathematical models in the parallel pore matrix are easier to solve than in the original structure of the porous material. The theoretical results in the parallel pore model are then fit to the experimental results in actual porous material, usually with average pore size and average tortuosity as the fitting parameters. The experimental procedure with nanochannels presented in this chapter offers a method to compare the theoretical results in parallel pore model to experimental results directly, without the introduction of fitting parameters, because the size and shape of the nanochannels are well defined. By excluding the arbitrary fitting parameters, the validity of the parallel pore model is easier to verify. Therefore, experimental results in nanochannels contribute to the improvement of the parallel pore model.

In conclusion, in this experiment, the measured results are highly repeatable with differ-

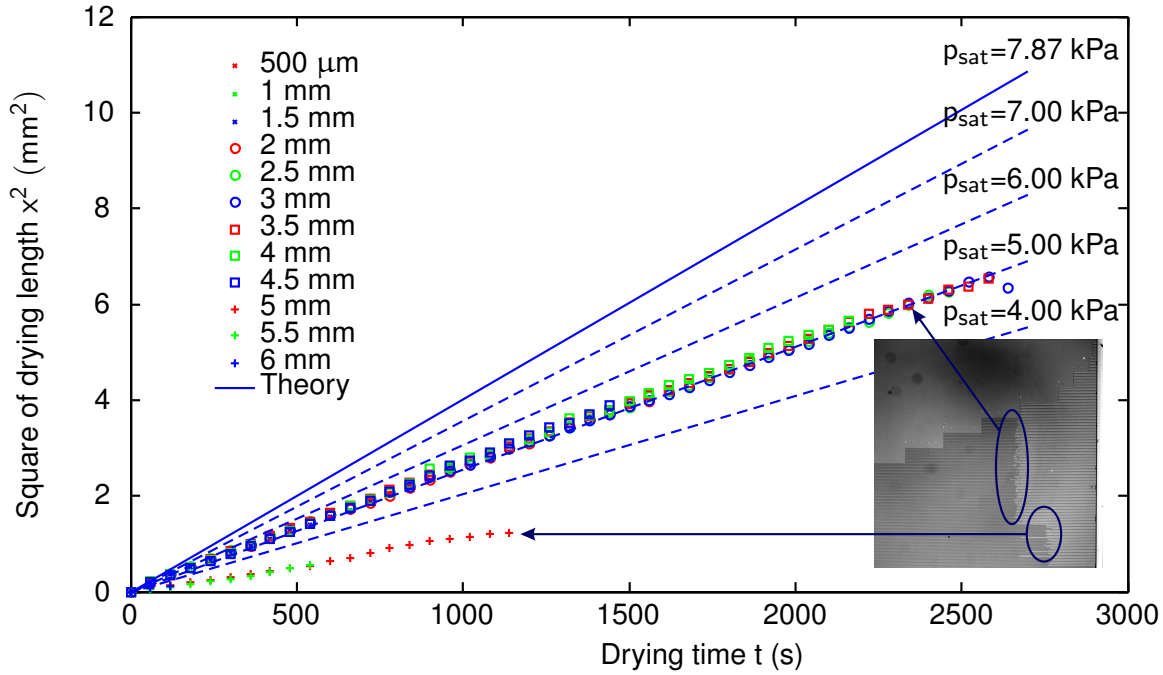


Figure 6.3: Square of measured drying lengths and theoretical prediction with different values of saturation pressure p_{sat} ($p_0 = 0$ Pa).

ent channels. The drying speed is found to be independent of the channel length. However, it is observed clearly that the fully filled channels dry with a higher speed than the partially filled channels. Highly linear relationship between the square of drying length and the drying time was observed, which agrees well with the theoretical model. However, it is important to experimentally confirm the level of exit partial vapour pressure. Better controlled experiments should be carried out to investigate the relation between the nitrogen flow and the drying speed. The lower drying speed of the partially filled channel should be explained by considering the absorption and desorption of gas in liquids.

6.3 Condensation in Nanochannels

6.3.1 Theoretical Analysis

The growth and the movement of a liquid column in condensation phenomenon are governed by the surface tension at two ends of the column and the rate of condensation. On the one hand, difference in radii of curvature at two ends leads to a net surface force, which

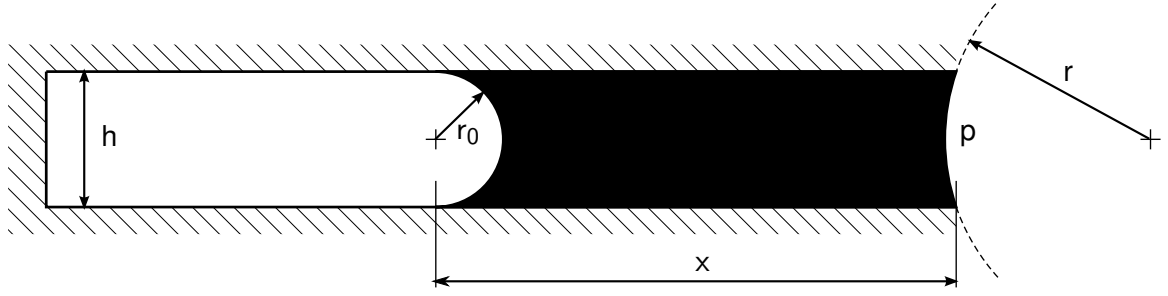


Figure 6.4: Model of a liquid column condensed at an open end of a slit-shaped nanochannel.

pulls the liquid column inside the nanochannel. On the other hand, the radius of curvature at the entrance of the nanochannel causes a drop in saturation vapour pressure, therefore induces the condensation. The value of radii of curvature at two ends of the column must satisfy the condition so that the growing rate of the liquid column due to condensation is equal to the advancing speed of the meniscus inside the nanochannel. In a planar nanochannel, the curvature of a meniscus is determined mainly by the channel height and not the channel width. Figure 6.4 describes a side view cross-section of a slit-shaped nanochannel with condensing liquid column forming at its entrance. At the entrance, the partial pressure of the vapour is p and the radius of curvature of the meniscus is r . At the other end of the column, where the radius of curvature is r_0 , the condensation or evaporation is assumed to be negligible. This condition is satisfied inside a long closed-end nanochannel, where the condensation and evaporation at the inner meniscus is balanced. If the fluid totally wets the wall of the channels, the radius of curvature r_0 is equal to half of the channel height h . According to Kelvin's law, the curvature of the meniscus at the open end leads to a drop in saturation vapour pressure. If the saturation vapour pressure drops below p , condensation happens at the open end. The rate of condensation is evaluated by Langmuir equation. Assume that the heat produced by the condensation process is totally dissipated (e.g. by a high velocity gas flow). Difference in curvatures at the two ends of the liquid column drives the fluid into the nanochannel. The growing rate of the liquid column is equal to the mass condensation rate at the open end. Force balance applied on the fluid column requires the total surface tension force to be equal to the viscous force:

$$2w\sigma \left(1 - \frac{h}{2r}\right) = \frac{12\mu w}{h} x \bar{u}. \quad (6.24)$$

Kelvin equation leads to the saturation vapour near a concave surface:

$$p'_{\text{sat}} = p_{\text{sat}} \exp \left(-\frac{\sigma V_M}{\mathcal{R}T} \right) . \quad (6.25)$$

Applying Taylor expansion and ignore terms higher than the second order:

$$p'_{\text{sat}} = p_{\text{sat}} - p_{\text{sat}} \frac{\sigma V_M}{\mathcal{R}T} . \quad (6.26)$$

Assuming that the radius of curvature r is on the order of r_0 , the meniscus surface area at the open end is:

$$A = \frac{\pi^2}{4} wh . \quad (6.27)$$

Mass condensation rate at the open end is given by Langmuir equation:

$$\dot{m} = \sqrt{\frac{M}{2\pi\mathcal{R}T}} (p - p'_{\text{sat}}) A . \quad (6.28)$$

From Eq. (6.28), the growing rate of the liquid column is:

$$\bar{u} = \frac{\dot{m}}{\rho wh} = \frac{\pi^2}{4} \frac{1}{\rho} \sqrt{\frac{M}{2\pi\mathcal{R}T}} \left(p - p_{\text{sat}} + p_{\text{sat}} \frac{\sigma V_M}{r\mathcal{R}T} \right) . \quad (6.29)$$

Equations (6.24) and (6.29) result in the equation system:

$$\begin{cases} x &= \frac{4}{\pi^2} \frac{h\sigma\rho}{12\mu} \sqrt{\frac{2\pi\mathcal{R}T}{M}} \frac{2r-h}{(p-p_{\text{sat}})r + p_{\text{sat}} \frac{\sigma V_M}{r\mathcal{R}T}} \\ \dot{x} &= \frac{4}{\pi^2} \frac{1}{\rho} \sqrt{\frac{M}{2\pi\mathcal{R}T}} \left(p - p_{\text{sat}} + p_{\text{sat}} \frac{\sigma V_M}{r\mathcal{R}T} \right) . \end{cases} \quad (6.30a)$$

$$\quad (6.30b)$$

Solving (6.30) with the initial condition $x|_{t=0} = 0$ results in:

$$x = x_0 \left(\sqrt{\frac{t}{\tau} + 1} - 1 \right) . \quad (6.31)$$

with

$$x_0 = \frac{4}{\pi^2} \frac{h^2 \sqrt{\pi\mathcal{R}T} \sqrt{\frac{\mathcal{R}T}{M}} \rho}{6\sqrt{2} V_M \mu p_{\text{sat}}} \quad (6.32)$$

and

$$\tau = \frac{16}{\pi^4} \frac{h^2 \pi (\mathcal{R}T)^2 \rho^3}{12M^2 \mu p_{\text{sat}} \left(p - p_{\text{sat}} + p_{\text{sat}} \frac{2\sigma V_M}{h\mathcal{R}T} \right)} . \quad (6.33)$$

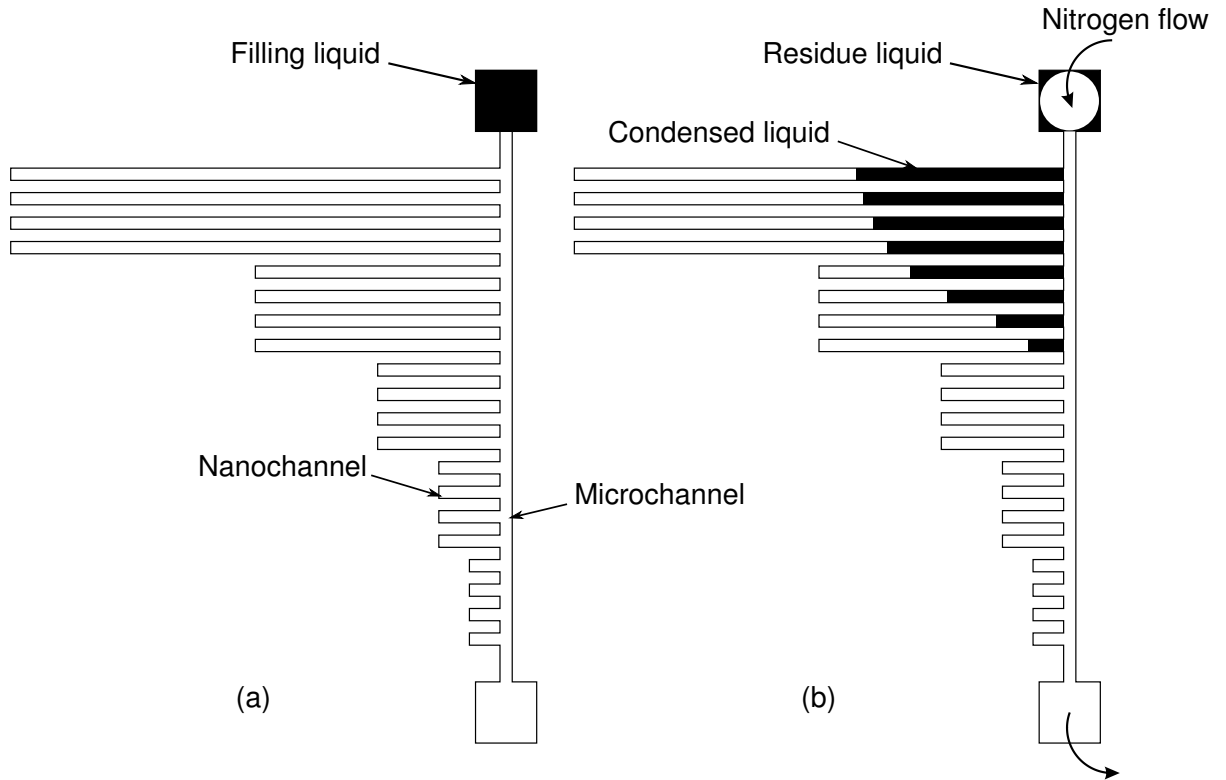


Figure 6.5: Condensation experiment set up, in this experiment, ethanol was used as the filling liquid: (a) Liquid fills in the reservoir; (b) Vapour evaporates from the liquid residue in the reservoir flow with Nitrogen in microchannel and condenses in nanochannels.

6.3.2 Experiments

Figure 6.5 presents the experimental set up for condensation. In this experiment, ethanol was used as the filling liquid. The vapour was collected from residue liquid left in the reservoir. The vapour in a nitrogen flow in the microchannel condensed in the nanochannels. The regions with condensed liquid in nanochannels darkened. The condensation process was observed and recorded with a microscope. The images were processed by a Matlab program to measure the filling distance versus time.

6.3.3 Results and Discussions

Figure 6.6 shows the theoretically expected growing length of the ethanol column at the entrance of the nanochannels with different vapour pressures in the microchannel. Figure 6.7 is generated by assuming a higher value of viscosity. With this assumption, the linearity of the theoretical line fits better to the experimental data.

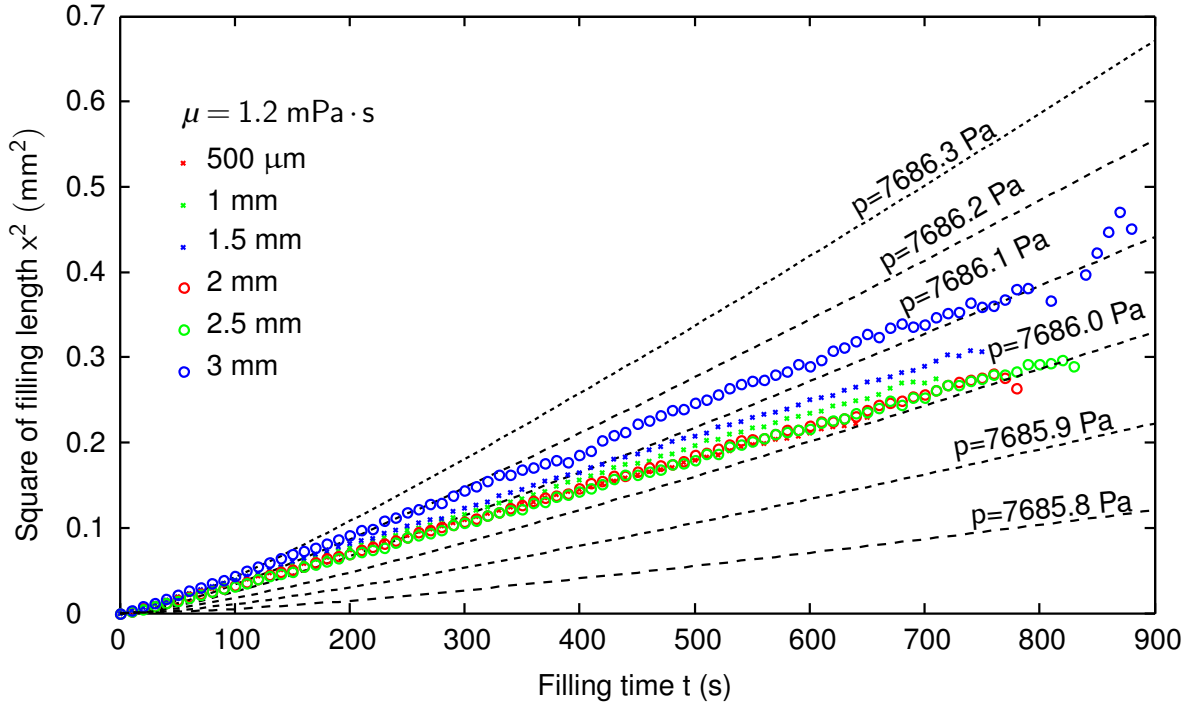


Figure 6.6: Square of filling length of ethanol versus time, compare to theoretical value, with bulk value of viscosity. Different types of data points represent different lengths of the nanochannels. The saturation vapour pressure is $p_{\text{sat}} = 7.87 \text{ kPa}$

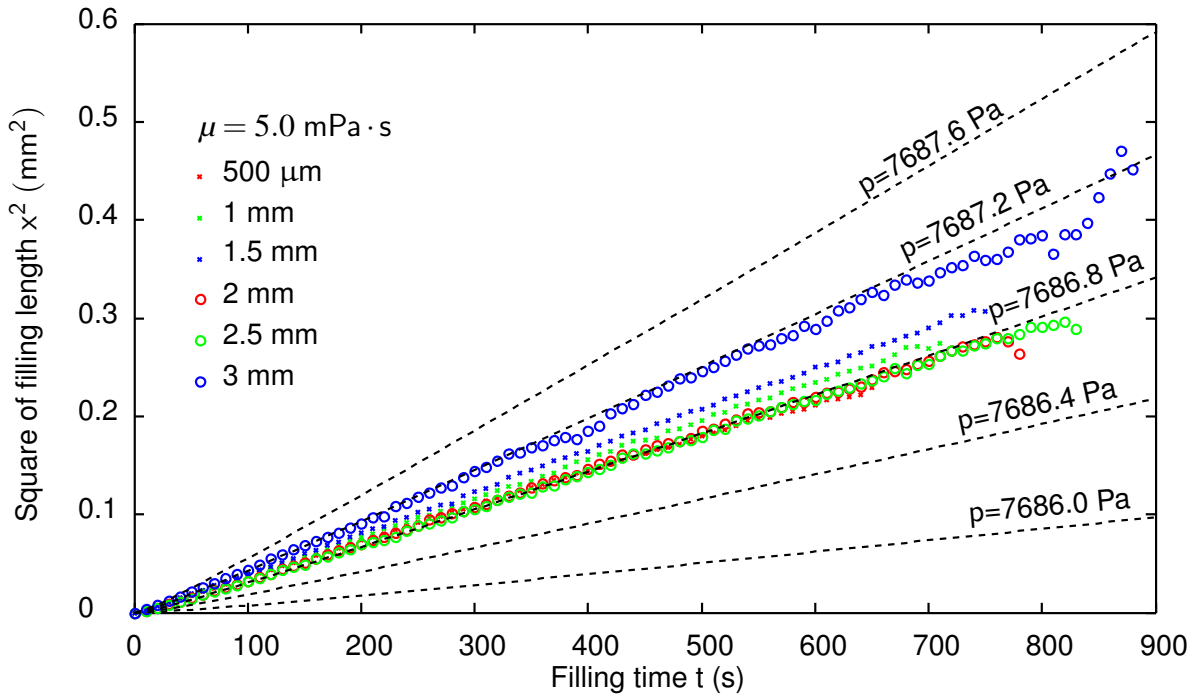


Figure 6.7: Square of filling length of ethanol versus filling time, compare to theoretical value, with higher viscosity $\mu = 5.0 \text{ mPa} \cdot \text{s}$ assumed.. Different types of data points represent different lengths of the nanochannels. The saturation vapour pressure is $p_{\text{sat}} = 7.87 \text{ kPa}$

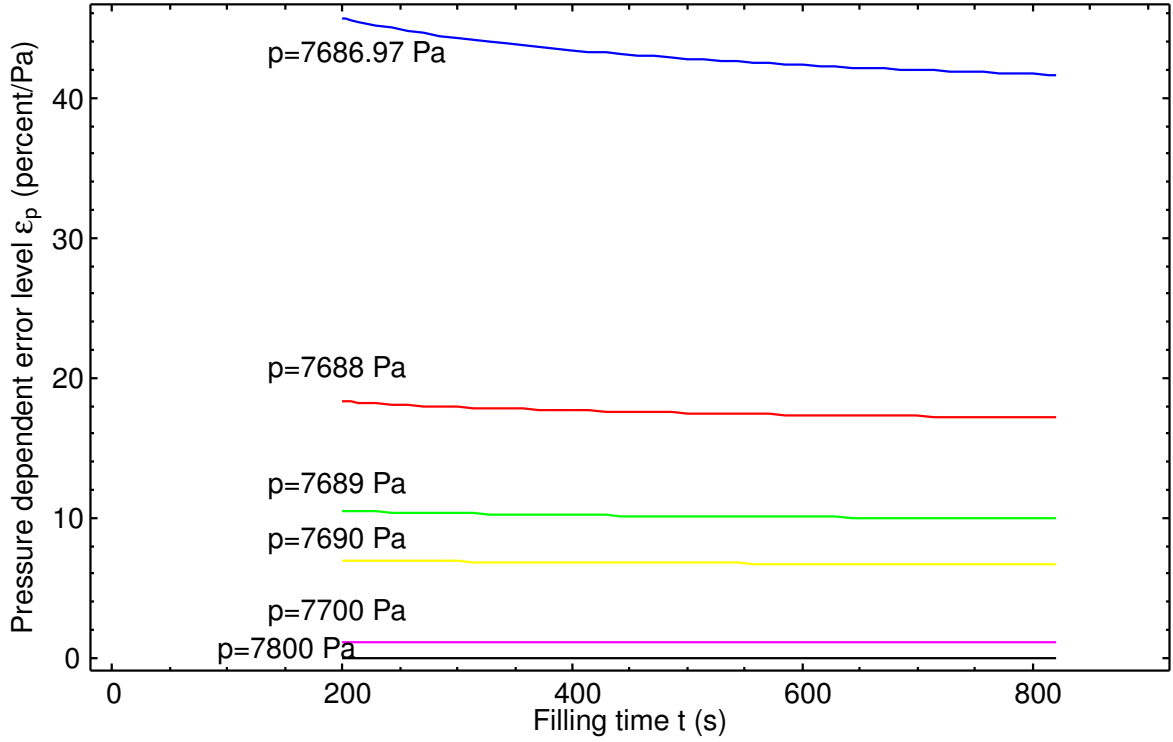


Figure 6.8: Dependence of error level of filling length on the change in vapour pressure at open end of the nanochannel.

In this experiment, the condensation length was less than 1 mm after 15 minutes. In comparison, the capillary filling length of ethanol in a nanochannel with a height of 45 nm is at the order of 100 mm after the same filling time, Eq. (4.60). The filling by condensation is significantly slower than by capillary.

To understand the stability of the filling process, the error level of the filling length is estimated as a function of the most significant parameters such as temperature and vapour pressure. The dependence of filling length on the vapour pressure at the entrance is represented by

$$\epsilon_p = \frac{1}{x} \frac{\partial x}{\partial p} \cdot 100\% . \quad (6.34)$$

This quantity indicates the error level in percentage corresponding to one Pa change in vapour pressure at the entrance. Figure 6.8 presents ϵ_p at several values of pressure p . It is showed that the filling length is highly sensitive to the vapour pressure at the open end.

The change in filling length depend on temperature both explicitly and through the change of saturation vapour pressure, as shown in Eq. (6.37). The term

$$\epsilon_T = \frac{1}{x} \frac{\partial x}{\partial T} \cdot 100\% \quad (6.35)$$

expresses the relative change in filling length with respect to temperature while

$$\epsilon_{\text{psat}} = \frac{1}{x} \frac{\partial x}{\partial p_{\text{sat}}} \cdot 100\% \quad (6.36)$$

expresses the relative change in filling length with respect to saturation vapour pressure. The values of these quantities represent the sensitivity of the filling length to temperature and saturation vapour pressure. The higher values of these quantities show that the filling length is more sensitive to temperature and saturation vapour pressure; and hence, a higher level of accuracy in temperature and saturation vapour pressure measurement is needed to analyse the condensation filling phenomenon.

$$\frac{\Delta x}{x} = \left(\frac{\partial x}{\partial T} + \frac{\partial x}{\partial p_{\text{sat}}} \frac{\partial p_{\text{sat}}}{\partial T} \right) \frac{\Delta T}{x} = \left(\epsilon_T + \epsilon_{\text{psat}} \frac{\partial p_{\text{sat}}}{\partial T} \right) \Delta T. \quad (6.37)$$

Figures 6.9 and 6.10 show ϵ_t and ϵ_{psat} respectively. Figure 6.11 shows empirical values of the saturation vapour pressure p_{sat} with respect to the temperature T , the values are obtained from [118]. At the conditions of our experiment, the fluctuation in temperature affects the filling rate mainly through the change of saturation vapour pressure. The hypothesis in this section, in some conditions, can explain the linear relationship between square of the filling length and the filling time, as observed in the experiments. However, to confirm this hypothesis, the vapour pressure at the open end of the nanochannels must be measured accurately. In this experiment, the values of vapour pressure at the open end were not determined. Some phenomena still have not been explained by the hypothesis, such as why the drying process and recondensation process can happen at the same time.

Recent research works reveal interesting results on the condensation filling in microchannels. The condensation in microchannels is a complicated process. Ma et. al. [121] pointed out that the condensation of steam in a microchannel may be in the form of an annular flow, droplet flow, injection flow, or intermittent flow. In contrast, the filling process due to condensation in nanochannels investigated in this work shows a better defined pattern. The filling length follows a quite simple relation versus time. This is a favourable behaviour for theoretical analyses. Preliminary estimation based on Kelvin's law and Langmuir's law fits well to the form of the filling data and the order of the filling speed.

Recondensation is an interesting phenomenon observed in nanochannels. Studying this phenomenon may reveal new aspects of the phase changing in nano scale. The phenomenon

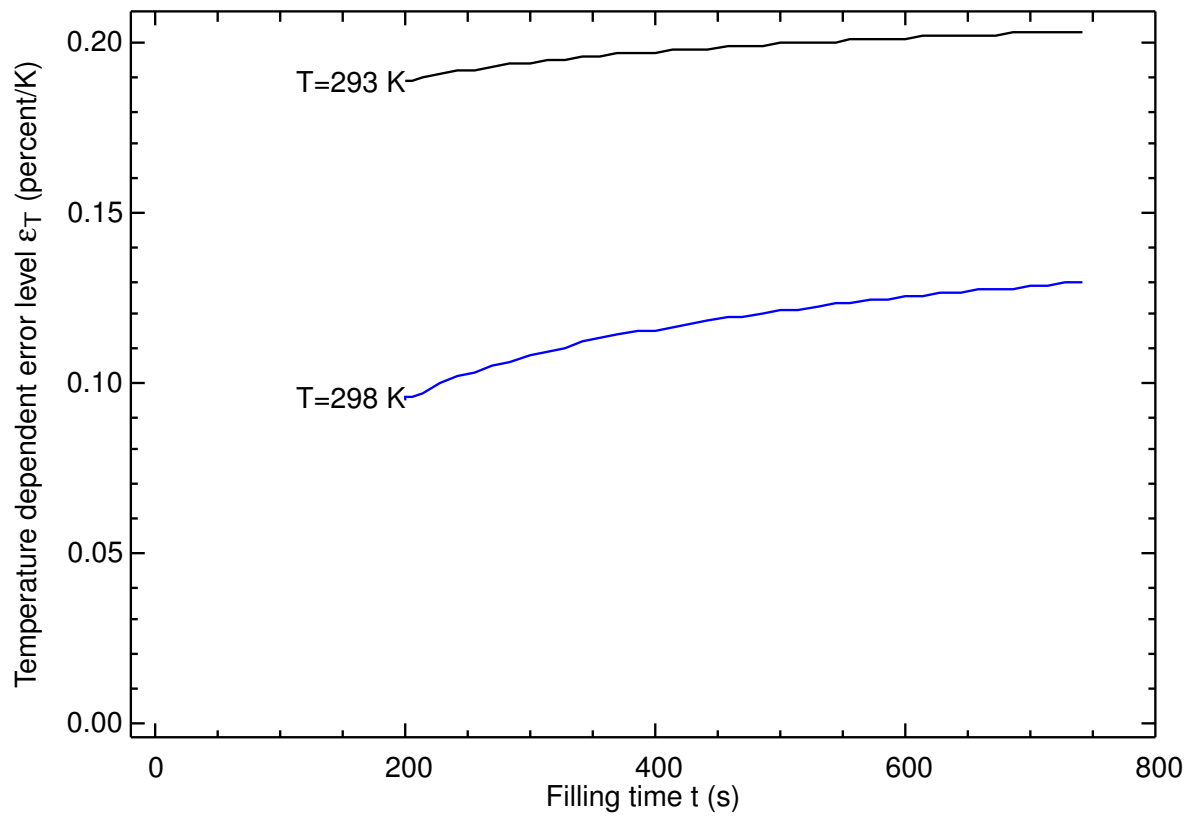


Figure 6.9: Explicit dependence of error level of filling length on the variation in temperature.

may highly depend on environmental parameters such as vapour pressure and temperature. Therefore, it is important to design more controlled experiment to quantitatively investigate this phenomenon.

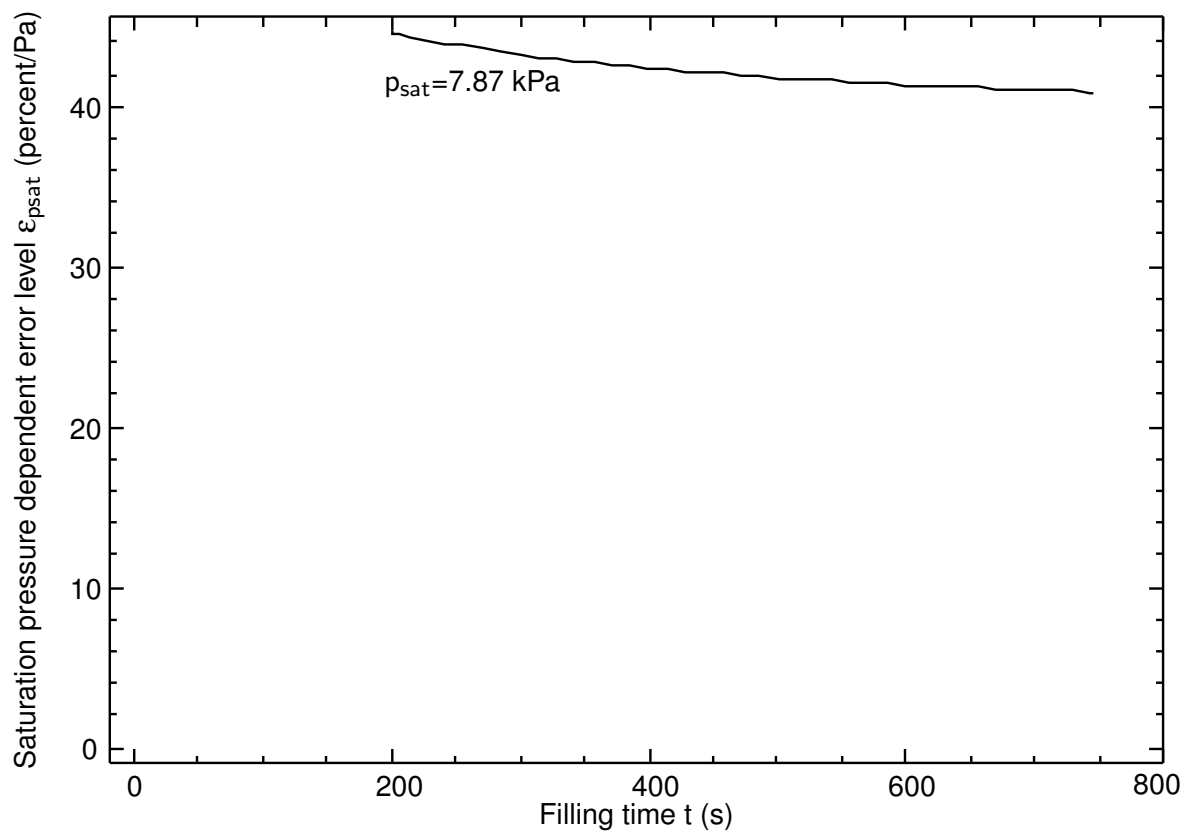


Figure 6.10: Dependence of error level of filling length on the variation in saturation vapour pressure.

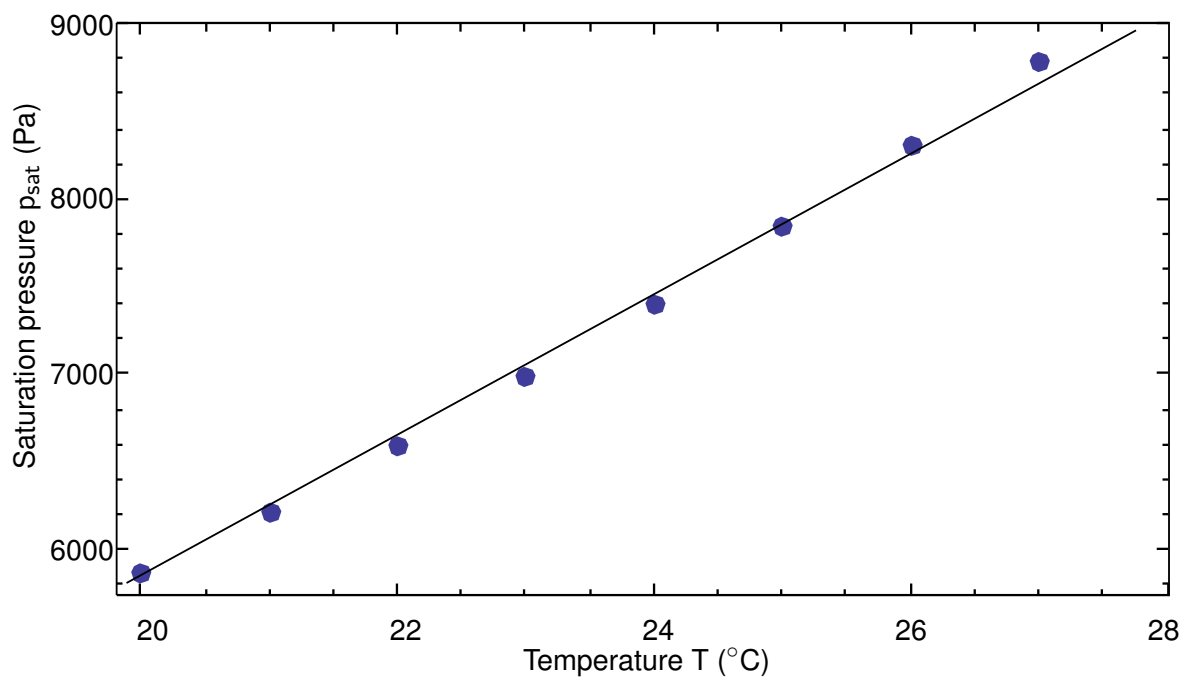


Figure 6.11: Saturation vapour pressure with various temperatures.

Chapter 7

Conclusions and Future Works

This thesis presents the fabrication of nanochannels and the investigation of transport phenomena in these nanochannels. The fabrication of silicon and polymeric nanochannels, capillary filling, gas absorption in liquid, evaporation and condensation in nanochannels were investigated. The experimental results were compared to theoretical values, predicted by models established in this work.

To prepare the experiments, nanochannels were fabricated using both silicon and polymeric materials. The silicon nanochannels and microchannels were fabricated by photolithography and Reactive Ion Etching (RIE) on a silicon wafer. The access holes were created by Deep Reactive Ion Etching (DRIE) from the back side of the wafer. The top of the nanochannels and microchannels was sealed by a Pyrex glass wafer using anodic bonding. Poly(methyl methacrylate) (PMMA) was used to fabricate polymeric nanochannels. The reservoirs were cut through the PMMA film by laser cutting. The nanochannels and microchannels were created on the surface of the PMMA film by hot embossing. The channel with a depth down to 30 nm can be fabricated by hot embossing technique. However, conventional thermal bonding at temperature higher than T_g cannot be used to assemble the components. Instead, low-temperature thermal bonding, enhanced by oxygen plasma surface treatment is proven to be useful. It is found that the durability of the devices depends on treatments to prevent delamination to initiate and to propagate. Another challenge in thermal bonding is to prevent distortion of nanostructure under the influence of pressure and temperature, especially at high stress region, such as convex edges or corners. This

distortion prevents reducing the size of nanostructure. Special compensation designs might be needed to overcome this problem.

To verify the significance of electroviscous effect, a mathematical model for capillary filling in nanochannels was developed. The model describes the charge distribution within the nanochannel during the capillary filling process. The electrostatic interaction and the surface tension at the advancing meniscus were taken into account. The asymptotic solution showed that the filling process followed Washburn equation with lower Washburn coefficient. Assuming that the surface tension and contact angle are the same as in bulk condition, the reduction of Washburn coefficient can be formulated by an increase in apparent viscosity. The apparent viscosity is the largest when the ratio between channel height, which is the smallest dimension of the channel, and the Debye length reaches an optimum value. A typical Debye length theoretically has values ranging from several nanometers to about one micrometer. Thus, for a dominant electroviscous effect, it is necessary to reduce and to precisely control the channel height. The apparent viscosity increases with high zeta potential and low molar conductivity or low ion mobility. The current results were obtained for a binary monovalent electrolyte in nanochannel with low zeta potential; however a similar approach can be used for other electrolyte and channel material. Experimental results revealed that capillary filling process in polymeric nanochannels obeys Washburn equation, with consideration of additional entrance resistance. However, the Washburn coefficient is significantly lower than predicted by classic Washburn equation, which is equivalent to an increase in apparent viscosity. The theoretical analysis of the electroviscous effect showed that this effect plays just a small role in the total increase of apparent viscosity. Consequently, there are other phenomena involved in the variation of Washburn coefficient. In some nanochannels, air bubbles formation is clearly observed, and possibly contributes in the reduction in Washburn coefficient. It is necessary to evaluate the characteristics of capillary filling with consideration of the air bubbles formation.

The experiments on capillary filling in closed-end nanochannels examine the interactions between liquid, gas and solid phases in nanochannels. The experiments were carried out in closed-end silicon nanochannels with different lengths. The experimental results showed that the process at first resembled the capillary filling process in open-end nanochannels. However, at the end of the filling process, the menisci did not stop at the value

predicted by the model without gas absorption, but continued to fill until the end of the nanochannels. The remaining gas trapped in the nanochannels dissolved in the liquid in the final stage of the filling process. A quantitative analysis of the experimental results at the end of the filling process showed a linear relationship between the filled area and the time. High magnification images reveal that air bubbles are captured by irregular movements of the air/liquid interfaces. Air bubbles reduce their sizes before totally disappear. A mathematical model was built with consideration of the gas absorption and diffusion, characterized by Henry's law and Fick's law respectively. The theoretical model explains well the experimental results. The experiment suggests that the dissolution of gas in the liquid is important in nanoscale, where the Laplace pressure is high. The dissolution phenomenon of gas in liquid can influence the transport of fluid in nanochannels.

To investigate the evaporation of fluid in nanochannels, ethanol and isopropanol were filled in closed-end nanochannels then dried with a nitrogen flow. The measurement results of drying of ethanol in nanochannels with different lengths were highly repeatable with different channel lengths. The drying speed was found independent on the total channel lengths. A theoretical model using diffusion process was built to describe the drying process. The experimental results qualitatively agree with the theoretical model. However, future experiments should aim to make a quantitative comparison to the theory and to improve this theory if necessary. In addition, the fully filled nanochannels dried faster than partially filled channels. This phenomenon may be due to the absorption and desorption of gas in liquids. This hypothesis should be confirmed in future works. The condensation of liquid in nanochannels was examined by blowing evaporated vapour across the entrance of the nanochannels. The condensation of liquid was observed. The meniscus of the condensed liquid slowly advances along the channels. The movement of the meniscus was explained by the difference in curvature of the menisci at two ends of the liquid column. In future, better controlled experiments should be established to verify the dependence between the condensation speed and the nitrogen flow, as well as the partial vapour pressure of the condensing liquid in vapour phase.

In conclusion, mass transport in nanochannels is a complicated process. Capillary filling, gas absorption, evaporation, and condensation of liquid are separated phenomena in macroscale. However in nanochannels, these phenomena usually happen simultaneously.

In addition, each phenomenon is also affected by the significant surface effect in nanochannels, such as EDL, corner flow or film flow. In order to analyse the individual phenomenon, it is essential to isolate one phenomenon from the others. In this thesis, experimental and theoretical investigations of above phenomena were presented. Although the general behaviours of liquid in each phenomenon were figured out, a fully quantitative analysis needs to be performed with better control of environmental parameters such as temperature and vapour pressure. Such investigations also require accurate sensing technology in nanoscale.

Publications

Journal Papers

1. V.N. Phan, C. Yang, and N.T. Nguyen. Analysis of capillary filling in nanochannels with electroviscous effects. *Microfluidics and Nanofluidics*, 7(4), 1-12, 2009.
2. V.N. Phan, N.T. Nguyen, C. Yang, P. Joseph, L. Djeghlaf, D. Bourrier, and A.M. Gué. Capillary filling in closed-end nanochannels. *Langmuir*, 26(16), 13251-13255, 2010.
3. V. N. Phan, N. T. Nguyen, C. Yang. Mass Transport in Nanochannels. *Micro and Nanosystems*, 2(4), 289-297, 2010.
4. V. N. Phan, P. Joseph, L. Djeghlaf, A. E. D. Allouch, D. Bourrier, P. Abgrall, A. M. Gue, C. Yang, N. T. Nguyen. Capillary Filling in Nanochannels - Modeling, Fabrication and Experiments. *Heat Transfer Engineering*, 32(7-8), 624-635, 2011.
5. V. N. Phan, N. T. Nguyen, C. Yang. Fabrication and experimental characterization of nanochannels. *ASME Journal of Heat Transfer*, 2012, DOI:10.1115/1.4005702.

Conference Papers

1. V.N. Phan, C. Yang, and N.T. Nguyen. Capillary filling in nanochannels. *Seventh International ASME Conference on Nanochannels, Microchannels and Minichannels, Pohang, South Korea, 2009.*

2. V.N. Phan, P. Abgrall, P. Shao, J.A. van Kan, and N.T. Nguyen. Fabrication of nanochannels on polymer thin film. *Seventh International ASME Conference on Nanochannels, Microchannels and Minichannels, Pohang, South Korea*, 2009.
3. V.N. Phan, N.T. Nguyen, and C. Yang. Fabrication and experimental characterization of nanochannels. *ASME 2009 Micro/Nanoscale Heat and Mass Transfer International Conference 2009, MNHMT2009*, 2010.

Chapters in Books

1. V.N. Phan, N.T. Nguyen, C. Yang., and P. Abgrall, 2011, Applications of Nanofluidics. In *Encyclopedia of Micro- and Nano-Fluidics*, Li, D., Ed. *Springer*, 2011.

Appendix A

Hot Embossing Using Polycarbonate Film

Nanochannels were also fabricated on PC (Polycarbonate, Goodfellow Ltd., England) film, with the same silicon mold used in Section 3.3.1. Open channels with a minimum width of 2.5 μm and 29.7 nm in depth were fabricated, Figs. A.2, A.3. Many defects were found on the surface of the PC film after hot embossing process. The shape and size of one typical defect is showed in Fig. A.4. Further investigation should be carried out to analyse on the formation of these defects.

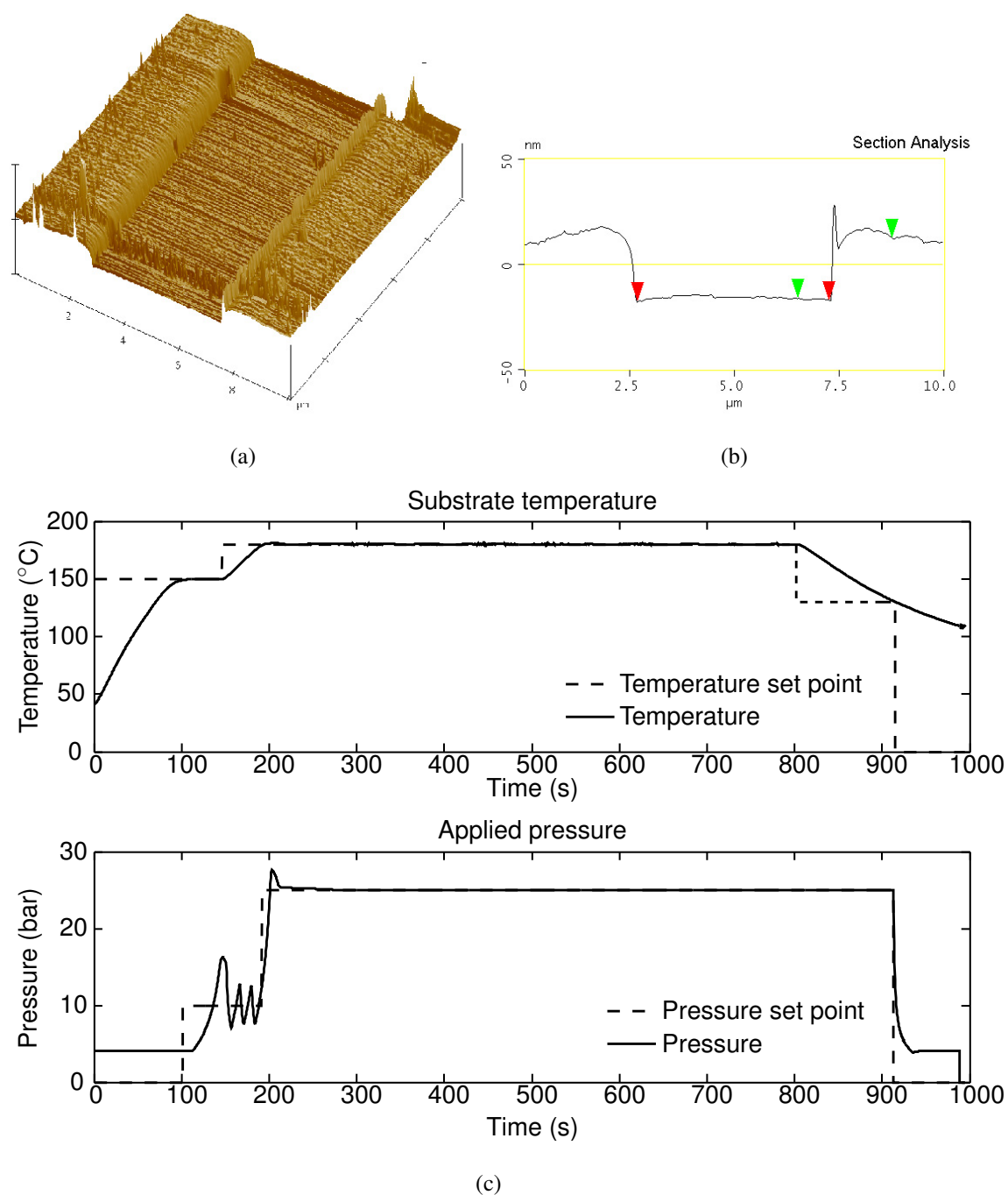


Figure A.1: An open channel created by hot embossing on PC film. The channel is $4.57\ \mu\text{m}$ in width and $28.6\ \text{nm}$ in depth: (a) 3D image; (b) Cross-sectional analysis; (c) Logged pressure and temperature of the process.

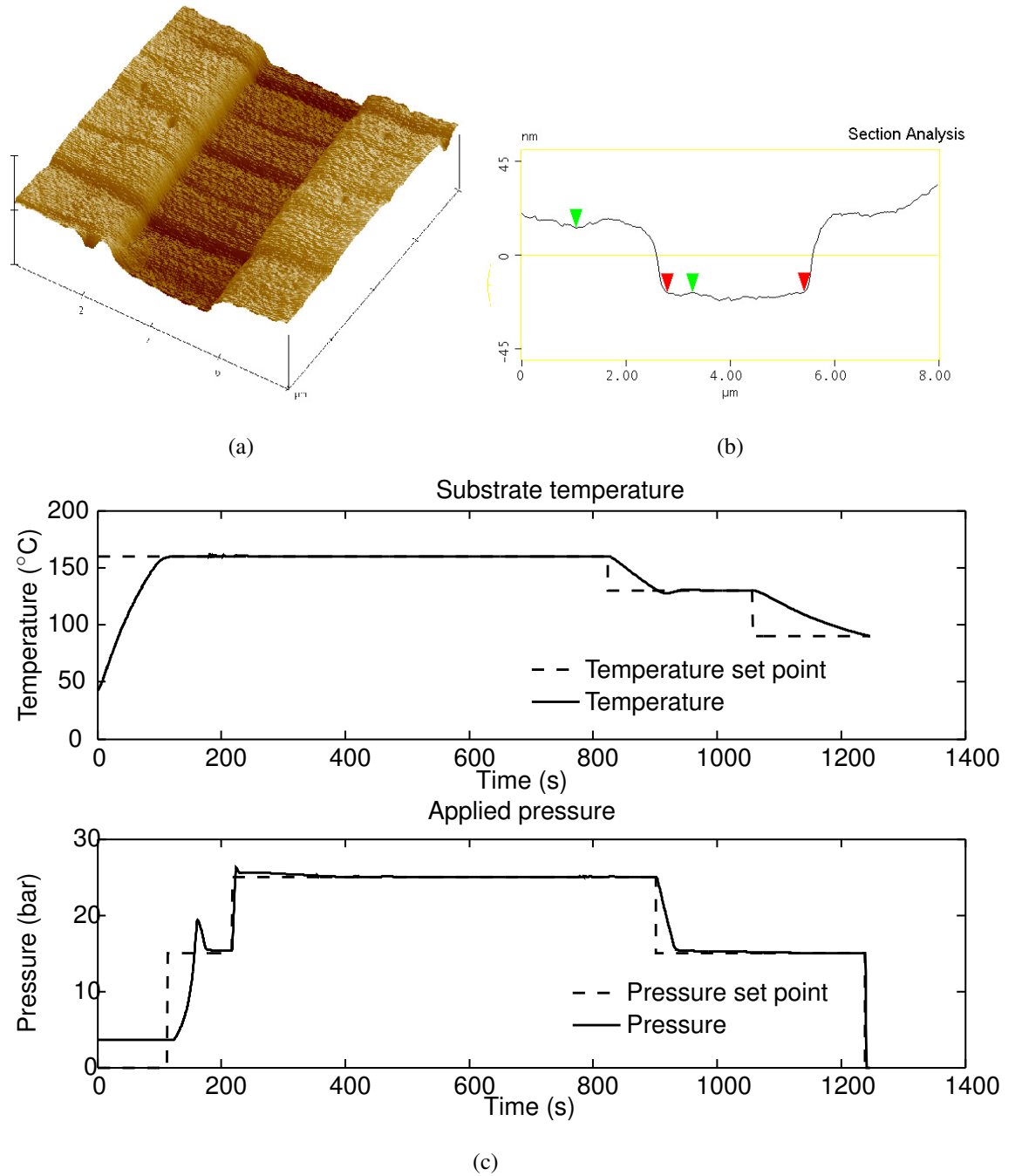


Figure A.2: An open channel created by hot embossing on PC film. The channel is $2.63\ \mu\text{m}$ in width and $30.8\ \text{nm}$ in depth: (a) 3D image; (b) Cross-sectional analysis; (c) Logged pressure and temperature of the process.

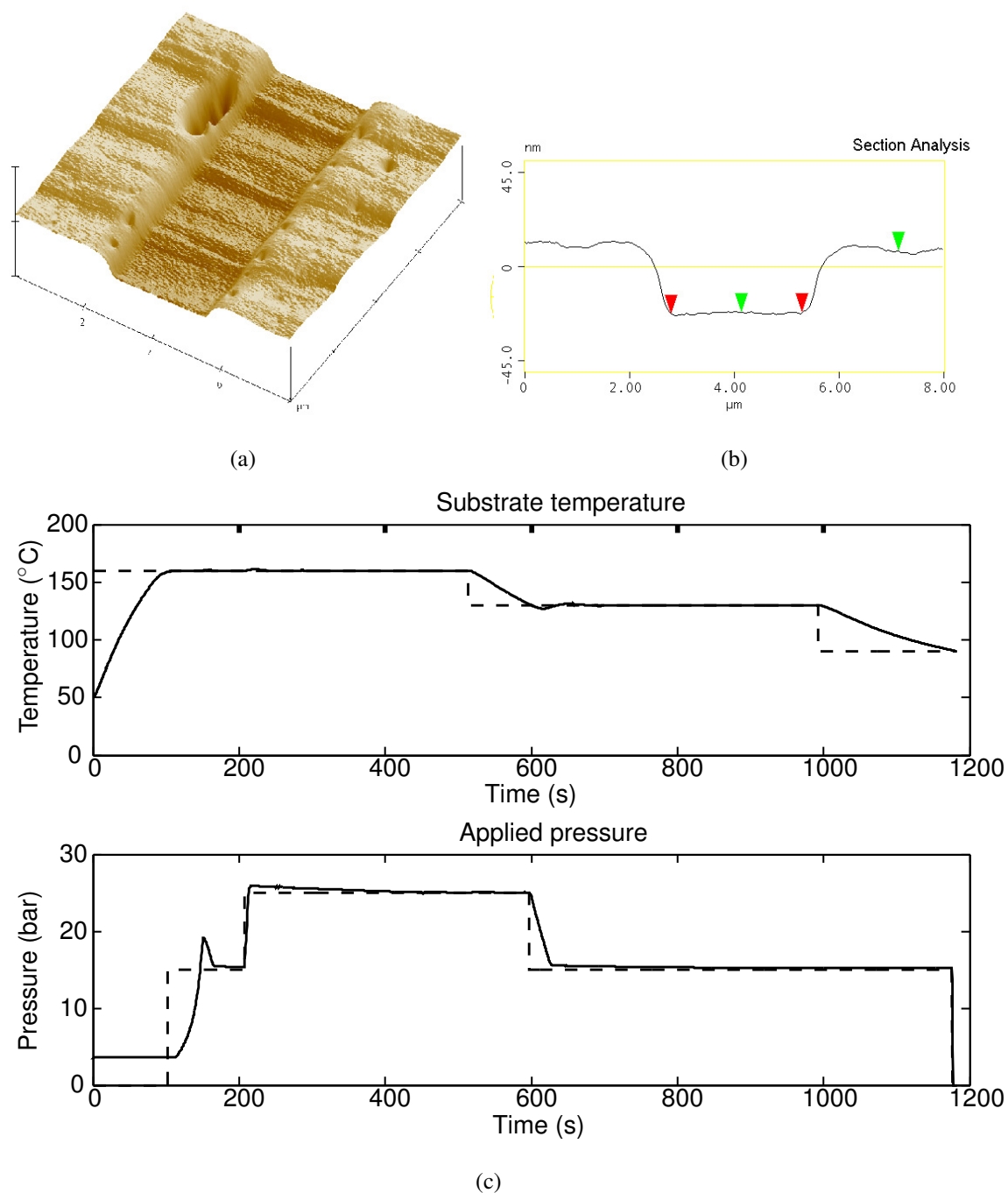


Figure A.3: An open channel created by hot embossing on PC film. The channel is $2.5\ \mu\text{m}$ in width and $29.7\ \text{nm}$ in depth: (a) 3D image; (b) Cross-sectional analysis; (c) Logged pressure and temperature of the process.

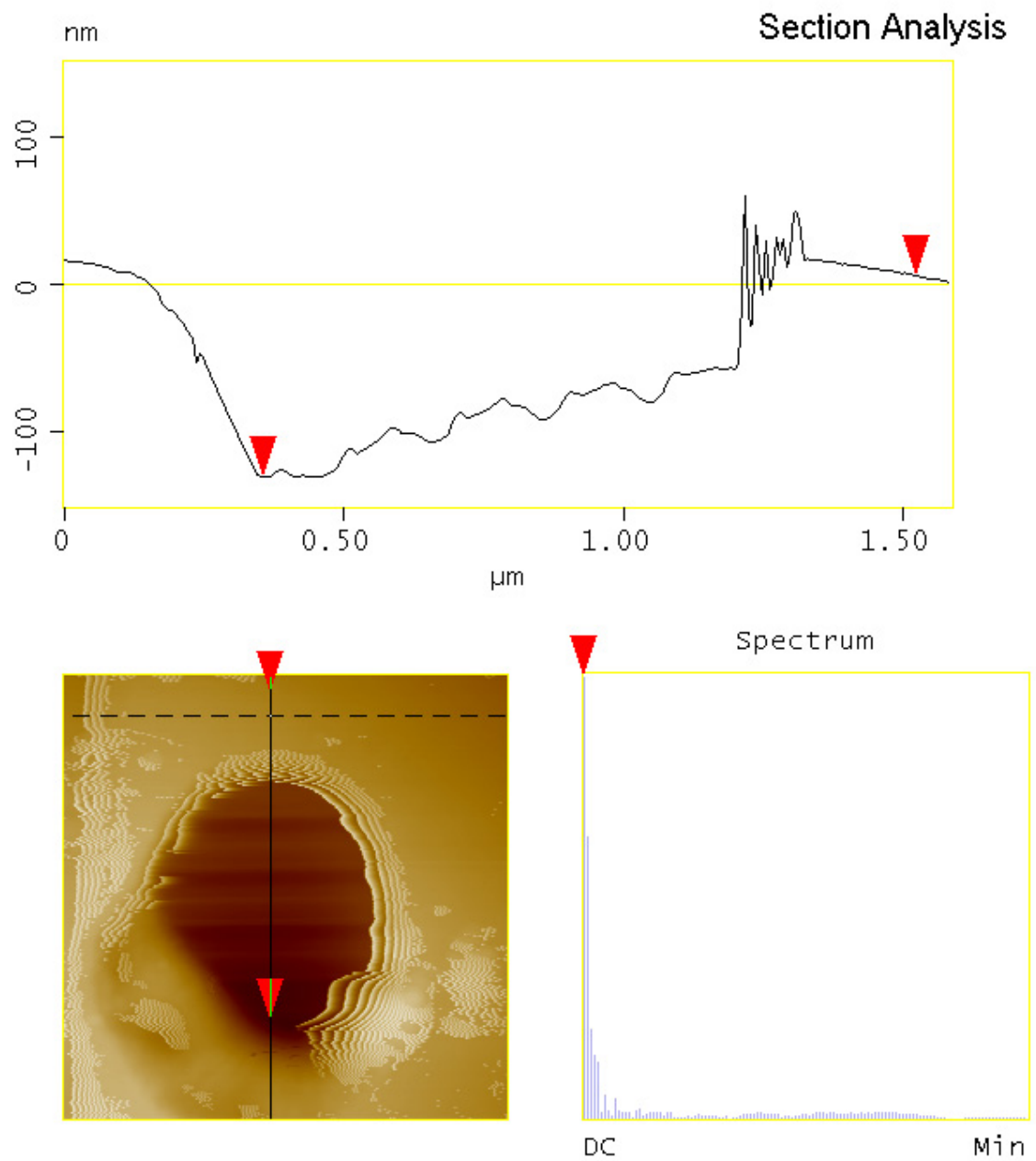


Figure A.4: Image of one defect found on the surface of the PC film after hot embossing process.

Appendix B

Stability of the Asymptotic Solution

To analyse the stability of the critical point found in Eq. (4.56), it is necessary to rewrite Eq. (4.52) as follows:

$$\begin{cases} \dot{\chi} &= \alpha(\chi, \xi, \bar{u}) = \frac{\hat{F}_s}{C} - \frac{A}{C}\chi - \frac{B}{C}\xi & \text{(B.1a)} \\ \dot{\xi} &= \beta(\chi, \xi, \bar{u}) = -D\xi + E\chi + \frac{\xi}{\chi}\bar{u}^2 & \text{(B.1b)} \\ \dot{\bar{u}} &= \gamma(\chi, \xi, \bar{u}) = \left[\left(\frac{\hat{F}_s}{C} - \frac{A}{C}\chi - \frac{B}{C}\xi \right) \frac{\chi}{\bar{u}} - \bar{u}\chi \right] \frac{\bar{u}^2}{\chi^2} . & \text{(B.1c)} \end{cases}$$

These equations cannot be linearized because γ_χ , γ_ξ , $\gamma_{\bar{u}}$ reduce to 0 when $\bar{u} = 0$. However, the stability still can be discovered by considering some experimental facts. Firstly, the capillary filling length x increases with time. Therefore, $\bar{u} = \dot{x}$ is a positive function. Secondly, the viscous force is proportional to $\bar{u}x$. Because the surface tension, as the capillary filling driving force, is a constant, the viscous force must be bound. The average velocity $\bar{u}$ must approach 0 when $t \rightarrow \infty$. The problem reduces to determining the stability of the critical point in $\bar{u} = 0$ hyperplane. With this condition, Eq. (B.1) can be rewritten as:

$$\begin{cases} \dot{\chi} &= \alpha(\chi, \xi, 0) = \frac{\hat{F}_s}{C} - \frac{A}{C}\chi - \frac{B}{C}\xi & \text{(B.2a)} \\ \dot{\xi} &= \beta(\chi, \xi, 0) = -D\xi + E\chi . & \text{(B.2b)} \end{cases}$$

To linearize this equation in $\bar{u} = 0$ hyperplane, the Jacobian matrix J is evaluated at the critical point:

$$J = \begin{bmatrix} \alpha_\chi & \alpha_\xi \\ \beta_\chi & \beta_\xi \end{bmatrix} = \begin{bmatrix} -\frac{A}{C} & -\frac{B}{C} \\ E & -D \end{bmatrix} . \quad \text{(B.3)}$$

The eigenvalues λ are calculated by:

$$\begin{vmatrix} -\frac{A}{C} - \lambda & -\frac{B}{C} \\ E & -D - \lambda \end{vmatrix} = \lambda^2 + \left(\frac{A}{C} + D\right)\lambda + \frac{AD + BE}{C} = 0. \quad (\text{B.4})$$

The discriminant Δ is

$$\begin{aligned} \Delta &= \left(\frac{A}{C} + D\right)^2 - 4\frac{AD + BE}{C} \\ &= \frac{A^2}{C^2} - 2\frac{AD}{C} + D^2 - 4\frac{BE}{C} \\ &= \left(\frac{A}{C} - D\right)^2 - 4\frac{BE}{C}. \end{aligned} \quad (\text{B.5})$$

It is necessary to know the sign of the reduced variables. By their definition, the variables A , C , and D are positive. Both variables B and E are opposite in sign to ζ , therefore, the product BE is positive.

As a result, if $\Delta > 0$, the two eigenvalues are:

$$\lambda_1 = \frac{1}{2} \left(-\frac{A}{C} - D - \sqrt{\Delta} \right) \quad (\text{B.6})$$

$$\lambda_2 = \frac{1}{2} \left(-\frac{A}{C} - D + \sqrt{\Delta} \right). \quad (\text{B.7})$$

With A , C and D are positive, λ_1 is obviously negative. In the quadratic equation (B.4):

$$\lambda_1 \lambda_2 = 4\frac{AD + BE}{C} > 0. \quad (\text{B.8})$$

Thus, λ_2 is also negative. The critical point is therefore a nodal sink and stable.

If $\Delta < 0$, two eigenvalues are complex numbers. The real parts are:

$$\Re(\lambda_1) = \Re(\lambda_2) = \frac{-A - D}{2C} < 0. \quad (\text{B.9})$$

The critical point is a spiral sink and stable.

Because there is only one finite critical point, and three variables χ , ξ , and $\bar{u}$ are bound as $t \rightarrow \infty$, the critical point in Eq. (4.56) describes the asymptotic solution of the system.

Appendix C

Experimental Data of Capillary Filling in Open-End Nanochannels

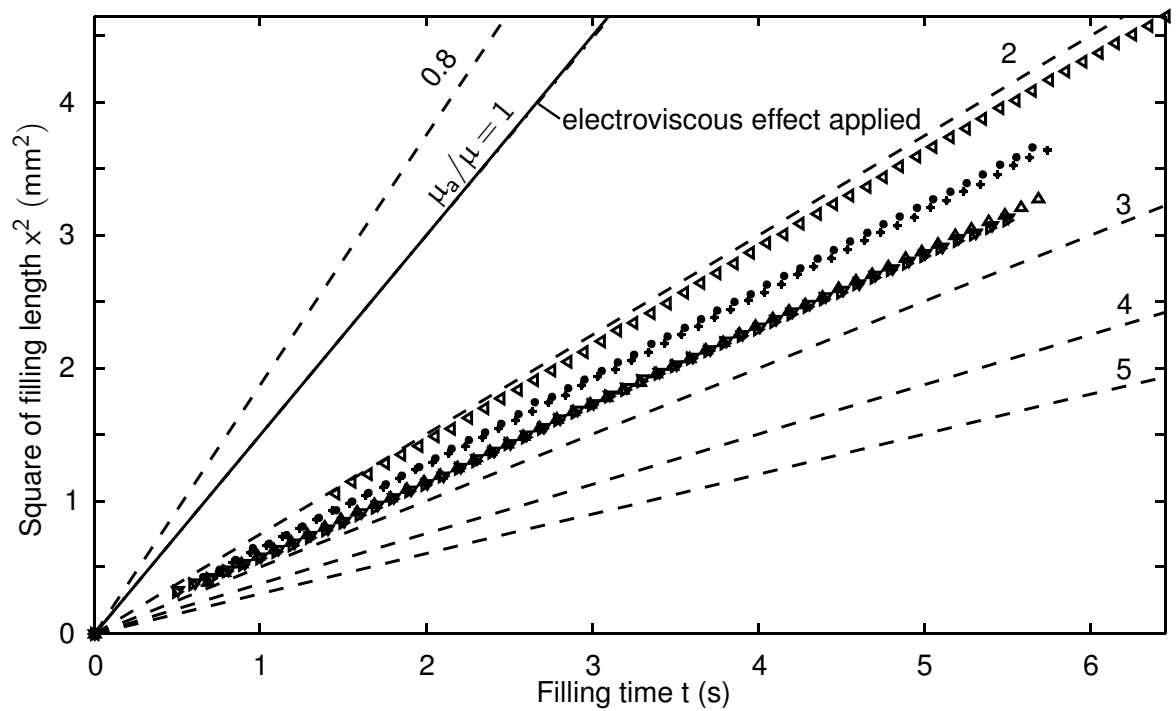


Figure C.1: Square of filling length of 0.001 M NaCl in nanochannels of 220 nm depth, 8.8 μm width.

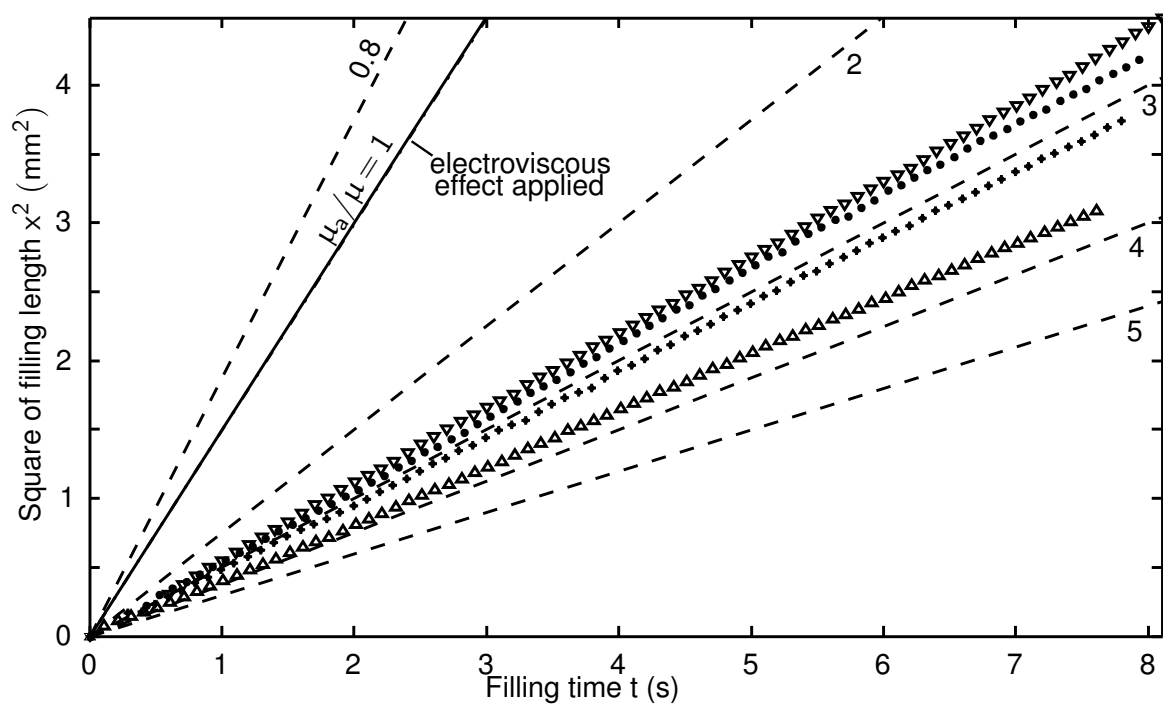


Figure C.2: Square of filling length of 0.001 M NaCl in nanochannels of 220 nm depth, 5 μ m width.

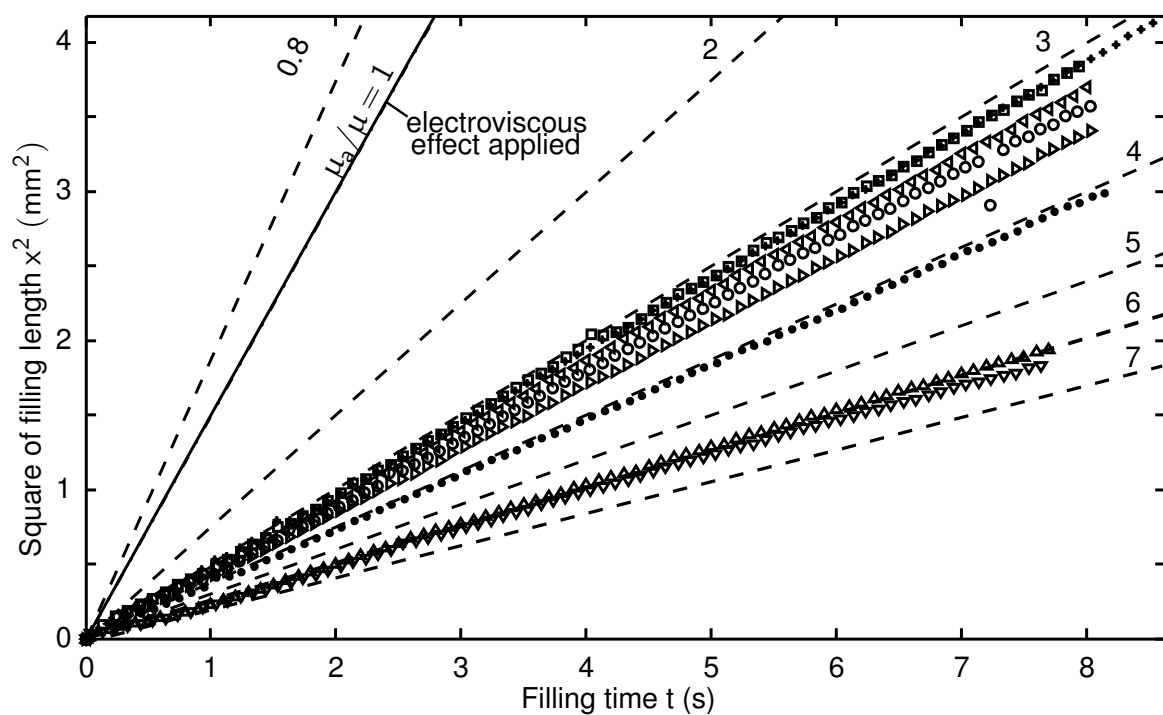


Figure C.3: Square of filling length of 0.001 M NaCl in nanochannels of 220 nm depth, 2 μ m width.

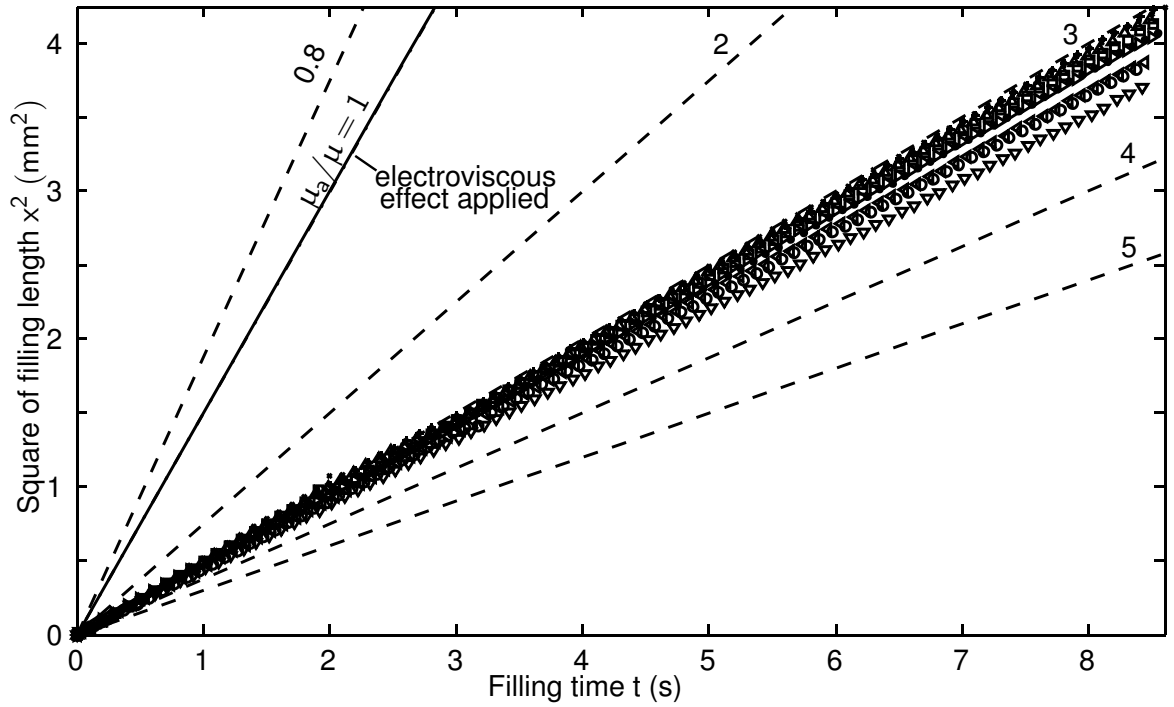


Figure C.4: Square of filling length of 0.01 M NaCl in nanochannels of 220 nm depth, 8.8 μm width.

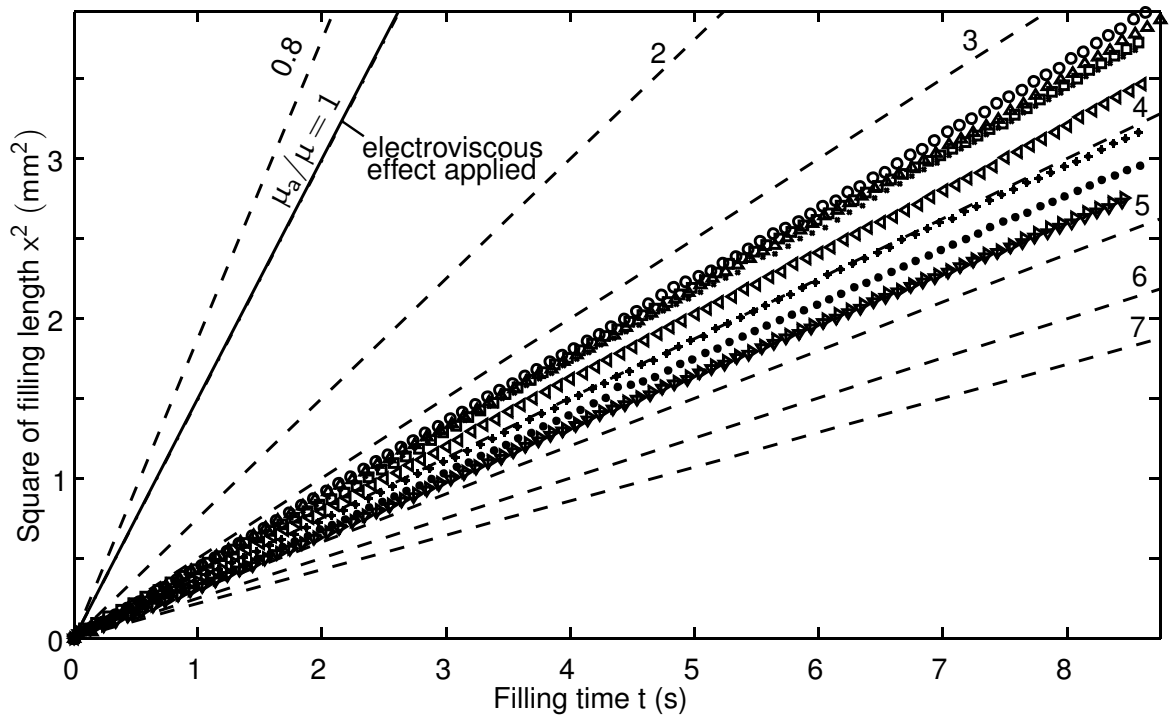


Figure C.5: Square of filling length of 0.01 M NaCl in nanochannels of 220 nm depth, 5 μm width.

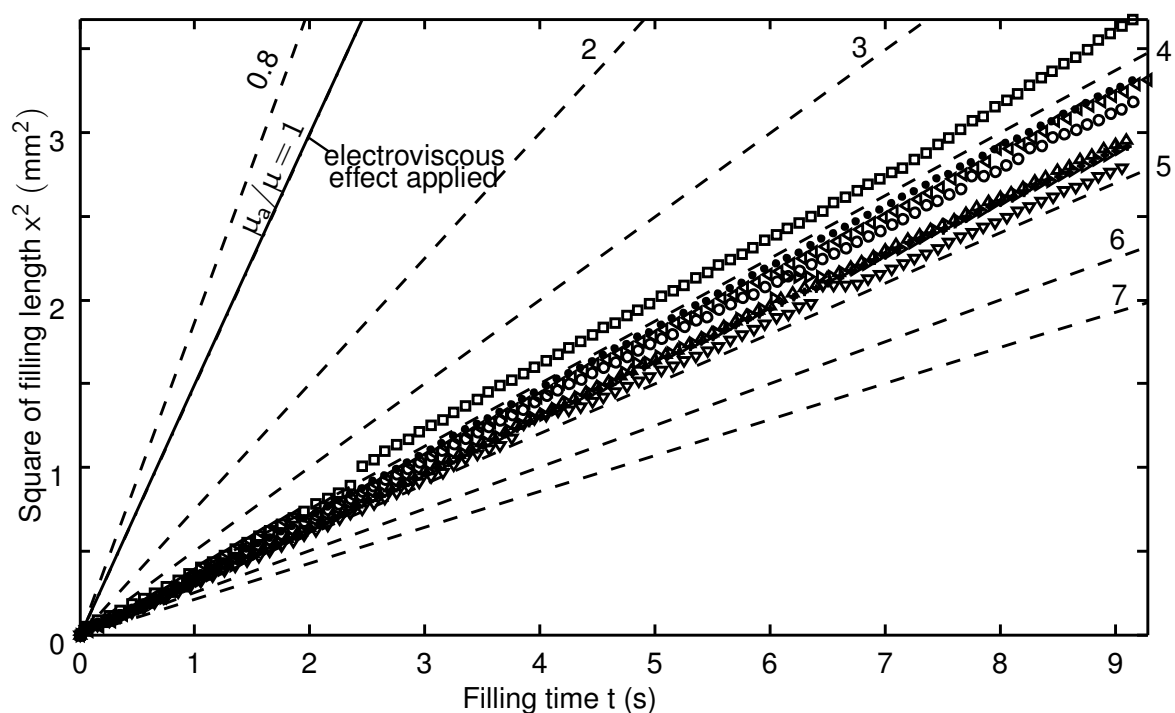


Figure C.6: Square of filling length of 0.01 M NaCl in nanochannels of 220 nm depth, 2 μ m width.

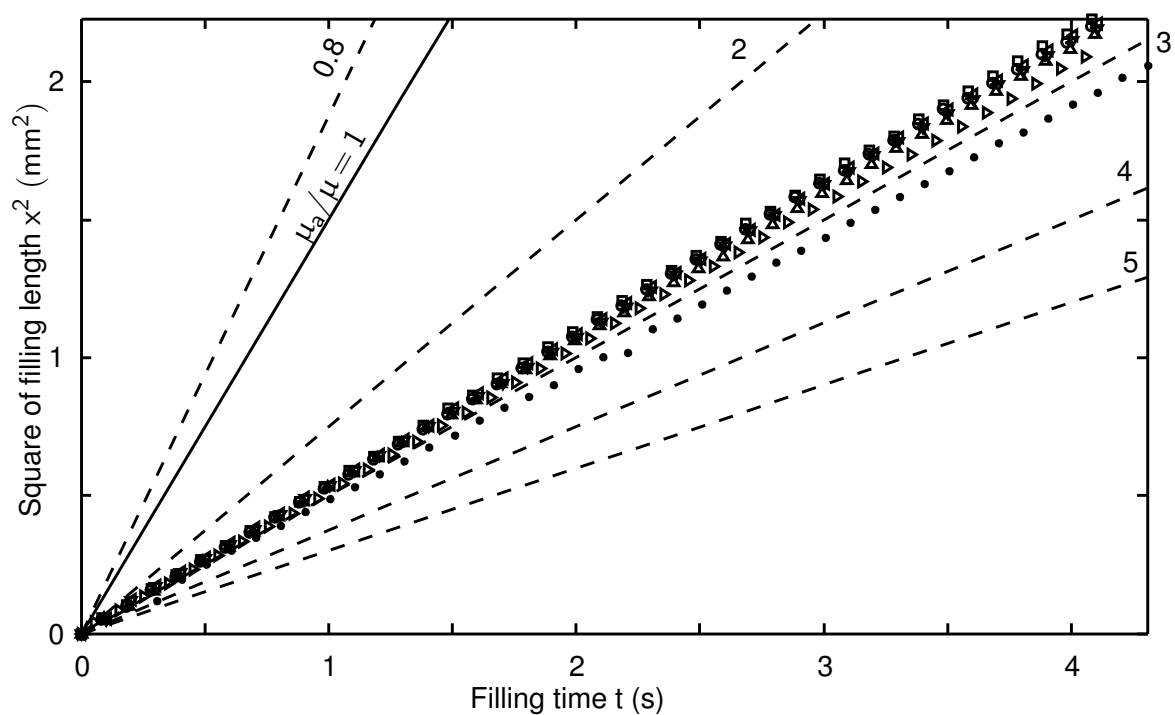


Figure C.7: Square of filling length of DIW in nanochannels of 220 nm depth, 5 μ m width.

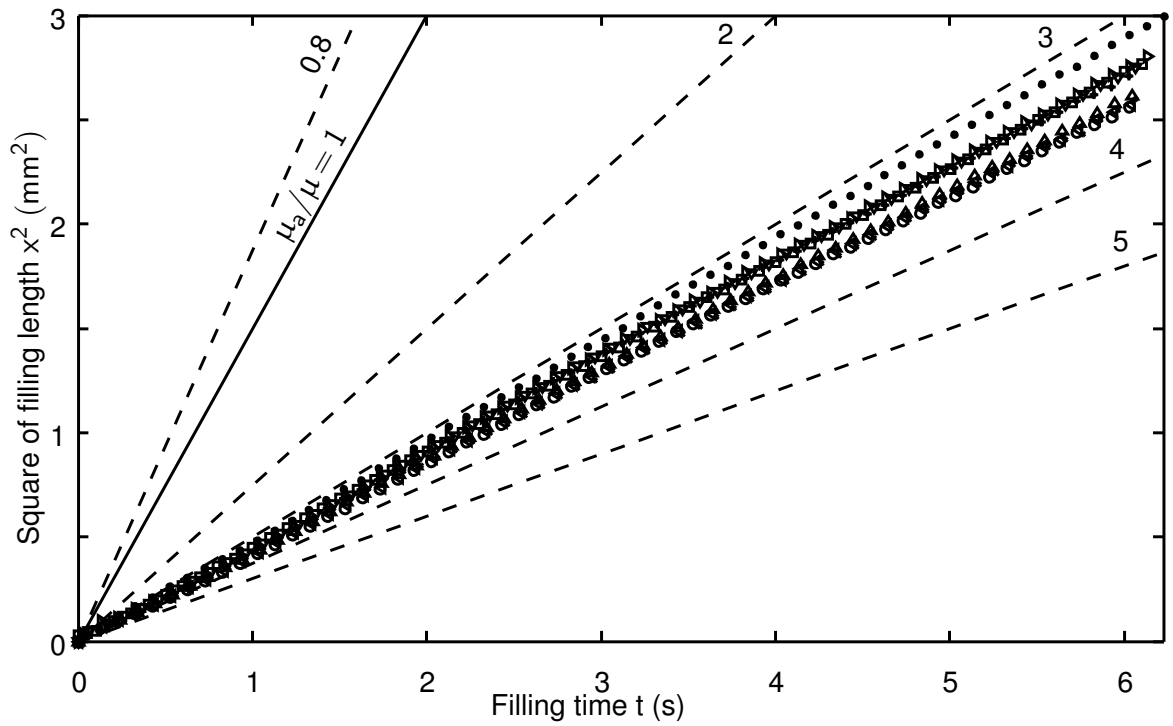


Figure C.8: Square of filling length of DIW in nanochannels of 220 nm depth, 2 μm width.

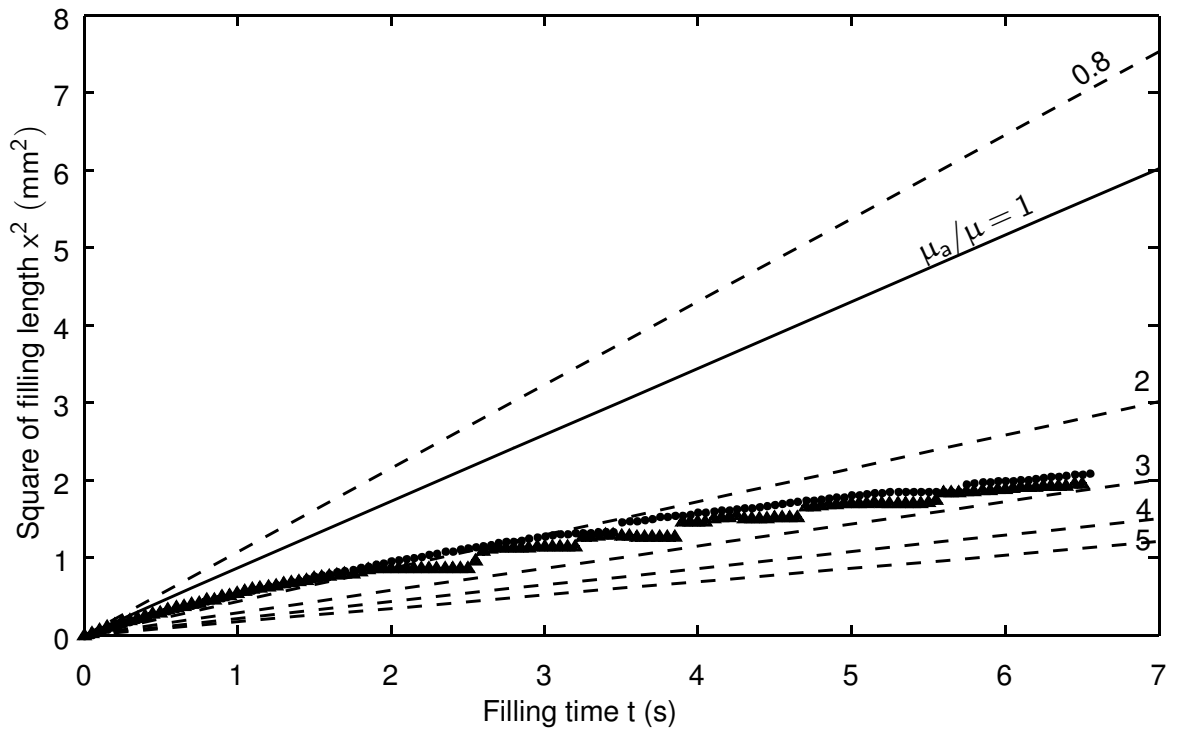


Figure C.9: Square of filling length of isopropanol in nanochannels of 220 nm depth, 8.8 μm width.

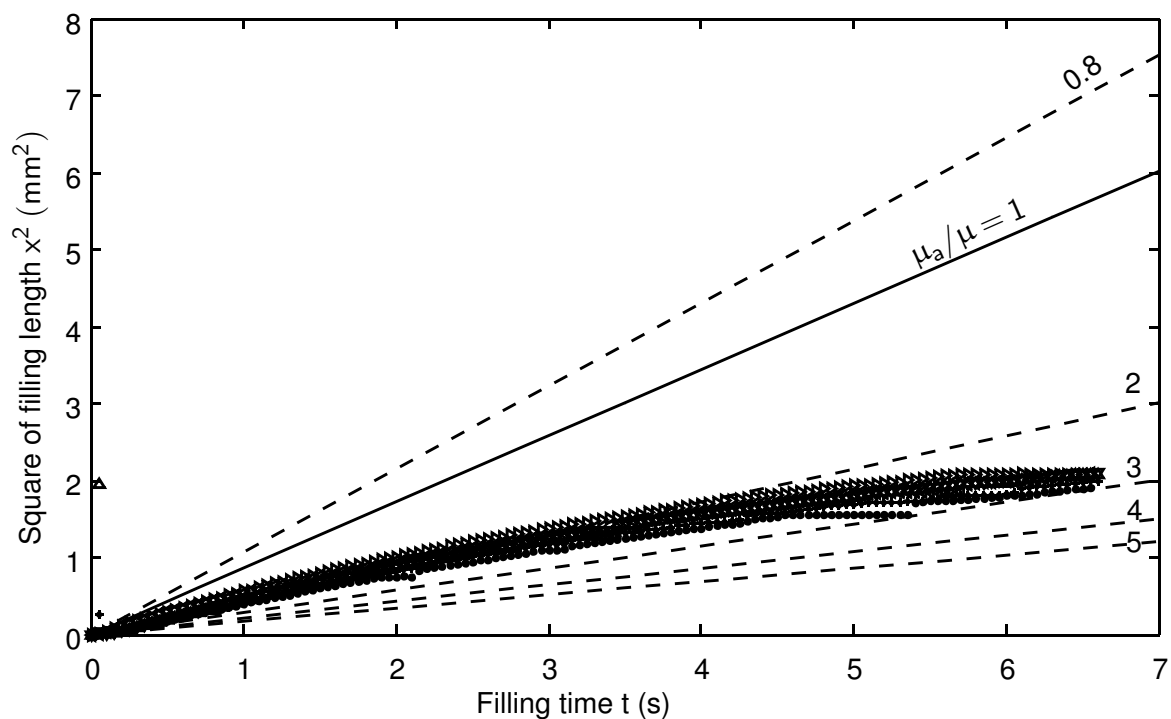


Figure C.10: Square of filling length of isopropanol in nanochannels of 220 nm depth, 5 μm width.

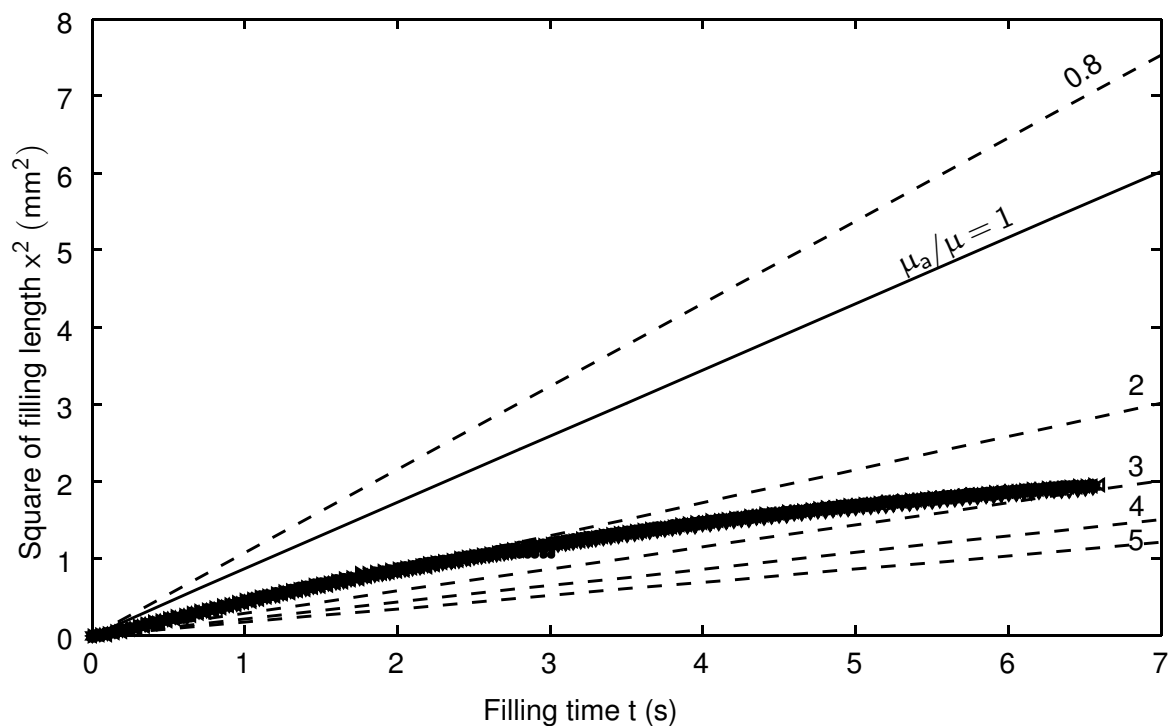


Figure C.11: Square of filling length of isopropanol in nanochannels of 220 nm depth, 2 μm width.

Appendix D

Filling Speed in Closed-End Nanochannels at the Second Filling Stage

As $m^* \rightarrow 0$ when $x^* \rightarrow 1$, limitation applied on Eq. (5.25) leads to the $\frac{0}{0}$ form. Applying l'Hôpital theorem on Eq. (5.25) results in:

$$\begin{aligned}
 \lim_{x^* \rightarrow 1} \frac{dx^*}{dt^*} &= \lim_{x^* \rightarrow 1} \frac{d \left[\alpha x^{*2} + \alpha m^* x^* + (1 - \alpha) x^* - 1 \right]}{d \left[x^{*2} - x^* \right]} \\
 &= \lim_{x^* \rightarrow 1} \frac{[2\alpha x^* + \alpha m^* + (1 - \alpha)] dx^* + \alpha x^* dm^*}{(2x^* - 1) dx^*} \\
 &= \lim_{x^* \rightarrow 1} \frac{[2\alpha x^* + \alpha m^* + (1 - \alpha)] \frac{dx^*}{dm^*} + \alpha x^*}{(2x^* - 1) \frac{dx^*}{dm^*}} \\
 &= \frac{(1 + \alpha) \lim_{x^* \rightarrow 1} \frac{dx^*}{dm^*} + \alpha}{\lim_{x^* \rightarrow 1} \frac{dx^*}{dm^*}} \\
 &= \frac{(1 + \alpha) X + \alpha}{X} \tag{D.1}
 \end{aligned}$$

with $X = \lim_{x^* \rightarrow 1} \frac{dx^*}{dm^*}$. Similarly, applying l'Hôpital theorem on Eq. (5.23b) gives:

$$\begin{aligned}
 \lim_{x^* \rightarrow 1} \frac{dm^*}{dt^*} &= \lim_{x^* \rightarrow 1} \beta \frac{d[1 - m^* - x^*]}{d[x^*(1 - x^*)]} \\
 &= \lim_{x^* \rightarrow 1} \beta \frac{dm^* + dx^*}{2x^* dx^* - dx^*} \\
 &= \lim_{x^* \rightarrow 1} \beta \frac{1 + \frac{dx^*}{dm^*}}{2x^* \frac{dx^*}{dm^*} - \frac{dx^*}{dm^*}}
 \end{aligned}$$

$$= \lim_{x^* \rightarrow 1} \beta \frac{1+X}{X} . \quad (\text{D.2})$$

To look for $X = \lim_{x^* \rightarrow 1} \frac{dx^*}{dm^*}$, dividing Eq. (5.25) by (5.23b) leads to:

$$\frac{\alpha x^{*2} + \alpha m^* x^* + (1 - \alpha) x^* - 1}{\beta [1 - m^* - x^*]} = - \frac{dx^*}{dm^*} . \quad (\text{D.3})$$

Applying l'Hôpital theorem on Eq. (D.3) gives:

$$\begin{aligned} - \lim_{x^* \rightarrow 1} \frac{dx^*}{dm^*} &= \lim_{x^* \rightarrow 1} \frac{d \left[\alpha x^{*2} + \alpha m^* x^* + (1 - \alpha) x^* - 1 \right]}{\beta d [1 - m^* - x^*]} \\ &= \lim_{x^* \rightarrow 1} \frac{[2\alpha x^* + \alpha m^* + (1 - \alpha)] dx^* + \alpha x^* dm^*}{-\beta (dm^* + dx^*)} \\ &= \lim_{x^* \rightarrow 1} \frac{[2\alpha x^* + \alpha m^* + (1 - \alpha)] \frac{dx^*}{dm^*} + \alpha x^*}{-\beta \left(1 + \frac{dx^*}{dm^*}\right)} . \end{aligned} \quad (\text{D.4})$$

The value of $X = \lim_{x^* \rightarrow 1} \frac{dx^*}{dm^*}$ is the solution of Eq. (D.5) at $x^* \rightarrow 1$ and $m^* \rightarrow 0$:

$$\begin{aligned} \beta X [1 + X] &= [2\alpha x^* + \alpha m^* + (1 - \alpha)] X + \alpha x^* \\ &= (1 + \alpha) X + \alpha . \end{aligned} \quad (\text{D.5})$$

In most cases, absorption and diffusion processes are quite slow, therefore the coefficient β is small. The right hand side of Eq. (D.5) is negligible. The approximated unique root of Eq. (D.5) is:

$$X = - \frac{\alpha}{1 + \alpha} . \quad (\text{D.6})$$

The filling speed at the end of the channel is derived from Eqs. (D.2) and (D.6) as:

$$\lim_{x^* \rightarrow 1} \frac{dx^*}{dt^*} = \frac{dx^*}{dm^*} \frac{dm^*}{dt^*} = X \beta \frac{1+X}{X} = \frac{\beta}{1 + \alpha} . \quad (\text{D.7})$$

For the more complicated case where β is large enough, for example in a smaller channel, an exact root of Eq. (D.5) is preferred. Equation (D.5) has then the form:

$$\begin{aligned} \beta X [1 + X] &= (1 + \alpha) X + \alpha \\ \Rightarrow \beta X^2 + (-1 - \alpha + \beta) X - \alpha &= 0 \end{aligned} \quad (\text{D.8})$$

where α and β are positive. Because the mass of trapped air reduces as the meniscus advances, the negative root of (D.8) is selected as:

$$X = \frac{1 + \alpha - \beta - \sqrt{4\alpha\beta + (-1 - \alpha + \beta)^2}}{2\beta} . \quad (\text{D.9})$$

Because (D.9) is one root of (D.8), substituting Eq. (D.9) into (D.1) gives:

$$\begin{aligned} \lim_{x^* \rightarrow 1} \frac{dx^*}{dt^*} &= \frac{(1 + \alpha)X + \alpha}{X} = \beta(1 + X) \\ &= \frac{1}{2} \left[1 + \alpha + \beta - \sqrt{4\alpha\beta + (-1 - \alpha + \beta)^2} \right] . \quad (\text{D.10}) \end{aligned}$$

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