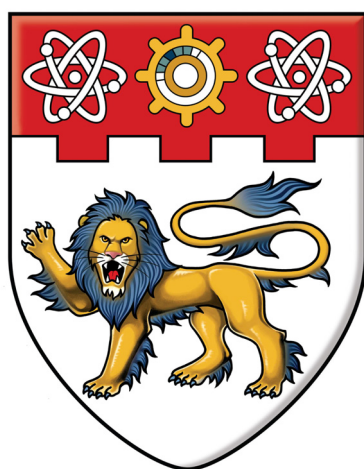


**THERMAL ASPECTS OF ELECTROKINETIC FLOW
AND CAPILLARY ELECTROPHORESIS IN
MICROCHANNEL NETWORK**



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**Thermal Aspects of Electrokinetic Flow and Capillary
Electrophoresis in Microchannel Network**

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ABSTRACT

Owing to numerous merits including improved resolution, increased throughput, reduced analysis time and decreased sample consumption, the microfluidic devices have found a wide spectrum of applications in the biomedical areas such as DNA sequencing, nucleic acid analysis, enzyme assays, immunoassays, etc. In microfluidic devices, electrokinetic transport, which in principle exploits two driving mechanisms - electrophoresis and electroosmosis, is used extensively to control liquid buffer flow and manipulate samples of nano/pico-liter volumes. It is known that the presence of Joule heating imposes limitations to the performance of electrokinetic transport. However, systematic investigations of the Joule heating and its effects on electroosmotic flow and electrokinetic mass transport based on the rigorous mathematical models still remain limited. In light of this, this dissertation provides a fundamental, systematic and in-depth exploration on the Joule heating and its effect on the electrokinetic transport in microfluidic systems.

Comprehensive mathematical models describing the electrokinetic mass transport in microfluidic systems with Joule heating effects are developed. The proposed models include the Poisson equation for the electric double layer (*EDL*) potential profile, the modified Navier-Stokes equation for the *EOF* velocity field, the conjugated energy equations for the Joule heating temperature fields in both liquid solution and channel walls, and the mass transport equation for the concentration distributions of sample species. Temperature-dependent electrical and thermophysical parameters are taken into consideration in these governing equations which are numerically solved using a finite difference based control-volume method. Specifically, a comparison of the numerical results obtained from (i) the widely used

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Power-law scheme, and (ii) the Crank-Nicolson scheme shows that use of the high-order Crank-Nicolson numerical scheme is necessary for numerical analysis of the time-dependent electrokinetic sample transport processes.

To investigate the applicability of the Boltzmann distribution derived on the basis of thermodynamic equilibrium and being employed by most researchers, the ionic concentration distributions are modeled using (i) the general Nernst-Planck equation and (ii) the Boltzmann distribution. It is found that that as for the Joule heating is concerned where the electrokinetic radius (κR) is large, the Boltzmann distribution can be assumed.

Numerical simulations are carried out for the Joule heating induced temperature field and its effects in cylindrical microcapillaries with thermostated cooling mode and in 3D rectangular cross-sectional microchannels with air natural convection cooling mode. The former is used in the commercial capillary electrophoresis systems and the latter is encountered in the fabricated microfluidic systems. The results demonstrate that due to the coupling between the electroosmotic flow field and the Joule heating induced temperature, the electroosmotic flow has almost the same entrance length as the temperature development. The Joule heating effect is significant for large-sized capillaries, concentrated buffer solutions, high applied electric field strengths, less effective cooling modes outside the channels, and small thickness and low thermal conductivity of substrates. It is also found that the presence of Joule heating has a great impact on the electroosmotic flow and sample species transport; it not only causes the electroosmotic flow to deviate from its normal flat profiles, but also makes the sample species transport faster axially as well as distort the sample flat interface for the sample translating interface and broaden the sample

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band and reduce the sample peak for the dispersion of a finite sample plug.

Moreover, electrokinetic sample mixing under Joule heating effects is studied numerically for T-shape microfluidic channels fabricated by (i) PDMA/PDMA substrates and (ii) Glass/PDMA substrates. The results show that the presence of Joule heating in general can enhance the sample mixing in T-shape channels. A more efficient mixing in PDMS/PDMA channels can be obtained as compared to that in Glass/PDMS channels.

To verify the proposed mathematical models, numerical scheme and program code, experiments are carried out using fabricated PDMS/PDMS and Glass/PDMS channels to study the Joule heating and its effects on electroosmotic flow. The liquid temperature field induced by Joule heating is measured using a rhodamine B based thermometry technique. The electroosmotic velocity field is characterized using a Micro-PIV technique. The experimental results are compared with the numerical predictions, and a reasonable agreement is obtained.

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NOMENCLATURE
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A	area (m^2)
B_1, B_2, B_3	dimensionless parameter
C	concentration of the electrolyte (M)
C_s	concentration of the sample specie (M)
c_p	specific heat capacity of the solution ($\text{J kg}^{-1} \text{K}^{-1}$)
$\vec{D}$	Displacement vector, (C m^{-2})
$D_i(T)$	diffusion coefficient of the i -th ions ($\text{m}^2 \text{s}^{-1}$)
$D_s(T)$	diffusion coefficient of the sample specie ($\text{m}^2 \text{s}^{-1}$)
D_T	diffusion coefficient due to the Taylor-Aris dispersion ($\text{m}^2 \text{s}^{-1}$)
$\vec{E}$	externally applied electric field strength vector (V m^{-1})
$\vec{E}_\psi$	electric field strength vector due to electrical double layer potential (V m^{-1})
E_r	externally applied electrical field strength in r , radial direction (V m^{-1})
E_x, E_y	externally applied electrical field strength in x and y direction
E_z	externally applied electrical field strength in z, axial direction for the cylindrical coordinates system; z direction for the Cartesian coordinate system (V m^{-1})
$\vec{F}_b$	total body force vector, N
$\vec{F}_s$	total surface force vector, N
e	fundamental charge ($1.602 \times 10^{-19} \text{ C}$)

NOMENCLATURE

H	height of the rectangular microchannels (m)
h	heat transfer coefficient ($W\ m^{-2}\ K^{-1}$)
$\vec{I}_t$	total electric current density vector ($A\ m^{-2}$)
$\vec{I}_d$	electric current density vector due to diffusion ($A\ m^{-2}$)
$\vec{I}_e$	electric current density vector due to electromigration ($A\ m^{-2}$)
$\vec{I}_c$	electric current density vector due to convection ($A\ m^{-2}$)
J	total flux for general variables (such as velocity and temperature etc)
Jo	Joule number
k_b	Boltzmann constant ($1.38 \times 10^{-23}\ J\ K^{-1}$)
$k_l(T)$	thermal conductivity of the electrolyte solution ($W\ m^{-1}\ K^{-1}$)
$k_s(T)$	thermal conductivity of the capillary wall ($W\ m^{-1}\ K^{-1}$)
L	length of the microchannels (m)
n_+, n_-	local number concentration of cations and anions, respectively (m^{-3})
n_0	bulk number concentration of ions in the electrolyte solution (m^{-3})
P	hydraulic pressure (Pa)
$\vec{P}_o$	Polarization vector, ($C\ m^{-2}$)
Pr	Prandtl number
q	heat flux ($W\ m^{-2}$)
$\dot{q}$	rate of Joule heat generation ($W\ m^{-3}$)
r	radial coordinate in cylindrical coordinate system
R	radius of the capillary (m)
Re	Reynolds number

NOMENCLATURE

S	source term in numerical scheme
Sc	Schmidt number
t	time (s)
T	temperature (K)
T_0	surrounding temperature (K)
u, v	electroosmotic flow velocity in axial and radial direction, for the cylindrical coordinate system; in x and y direction for the Cartesian coordinate system (m s^{-1})
u_{ep}, v_{ep}	electrophoretic velocity of the sample specie in axial and radial direction for the cylindrical coordinate system; in x and y direction for the Cartesian coordinate system (m s^{-1})
W	width of the rectangular microchannels (m)
w	electroosmotic flow velocity in the z direction in the Cartesian coordinate system (m s^{-1})
w_{ep}	electrophoretic velocity of the sample specie in the z direction in the Cartesian coordinate system (m s^{-1})
x, y	coordinate in Cartesian coordinate system
z	axial coordinate in cylindrical coordinate system; z coordinate in Cartesian coordinate system

Greek symbols

Γ	common diffusion coefficient for general variables in numerical scheme

NOMENCLATURE

α	thermal diffusivity ($\text{m}^2 \text{s}^{-1}$)
χ	electric susceptibility of the solution
ε_0	permittivity of vacuum ($8.85 \times 10^{-12} \text{ C V}^{-1} \text{ m}^{-1}$)
$\varepsilon(T)$	dielectric constant of the electrolyte
ε_r	relative dielectric constant of the electrolyte
ζ	zeta potential (V)
η_+, η_-	molar number of cations and anions in the electrolyte, respectively (M)
κ	Debye-Hückel parameter (m^{-1})
λ	electrical conductivity of the electrolyte (S m^{-1})
λ_+, λ_-	equivalent ionic conductivity of cations and anions, respectively ($\text{m}^2 \text{S mol}^{-1}$)
$\mu(T)$	viscosity of the electrolyte (Pa s)
μ_{ep}	electrophoretic mobility of sample specie in axial direction for the cylindrical coordinates system; in x direction for the Cartesian coordinate system ($\text{m}^2 \text{V}^{-1} \text{s}^{-1}$)
ν	kinematic viscosity of the electrolyte ($\text{m}^2 \text{s}^{-1}$)
ν_{ep}	electrophoretic mobility of sample specie in radial direction for the cylindrical coordinates system; in y direction for the Cartesian coordinate system ($\text{m}^2 \text{V}^{-1} \text{s}^{-1}$)
ω_{ep}	electrophoretic mobility of sample specie in z direction ($\text{m}^2 \text{V}^{-1} \text{s}^{-1}$)
σ	valence of the ions of the electrolyte
ρ	density of the electrolyte solution (kg m^{-3})

NOMENCLATURE

ρ_e	local net electrical charge density in the electric double layer (EDL) (C m ⁻³)
Φ_{th}	thermal viscous dissipation (W m ⁻³)
Φ	general variable in numerical scheme
ϕ	externally applied electric potential, (V)
ψ	local electrical double layer potential (EDL) (V)

Subscript

0	value of the variables at room temperature
<i>ref</i>	reference parameters
<i>e, w, n, s, p, t, b</i>	control volume interfaces in numerical scheme
<i>nb</i>	neighbor nodes in numerical scheme
<i>i</i>	the i-th ionic species or sample species
<i>x, y, z</i>	variable components in x, y, z direction in Cartesian coordinate system.
<i>r, z</i>	variable components in radial and axial direction in cylindrical coordinate system.

Superscript

*	value of cross section average for variables
—	dimensionless variables

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CHAPTER 1 INTRODUCTION

1.1 Background and motivation

Miniaturization and automation have revolutionized the world of microelectronics. In recent decades, these cutting-edge engineering technologies have been applied to the needs of the biomedical industry, giving rise to a brand new interdisciplinary area – Microfluidics. Microfluidic devices hold great promise for biomedical applications. They consume sample material and reagents in extremely low volumes. Individual microfluidic device can be inexpensive and disposable. The process time from sampling to result tends to be very short. And the most advanced chip designs can perform all analytical functions, including sample manipulation (*Minerick et al.*, 2003), sample pretreatment (*Peled*, 1996), separation, dilution, mixing (*Ben and Chang*, 2002; *Takhistov et al.*, 2003), ejection (*Thamida and Chang*, 2002), chemical reactions (*Northrup et al.*, 1995), and detection (*Meinhart et al.*, 1998) in a single integrated microfluidic circuit.

In principle, electroosmosis and electrophoresis are two kernel electrokinetic transport mechanisms used in the microfluidic devices. Electrophoresis refers to the migration of charged particles within an electrolyte solution relative to the fluid molecules under the influence of an applied electric field; while electroosmosis or electroosmotic flow (EOF), the complement of electrophoresis, refers to a liquid flow induced by imposing an external electric field along an electrostatically charged capillary. The advantages of using electrophoresis in capillaries were highlighted since the work of *Jorgenson and Lukacs* (1981, 1983), who popularized the use of capillary electrophoresis (CE) in the early 1980's. Since then, prolific research on

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capillary electrophoresis with a wide spectrum of applications has been reported (*Wang and Fang*, 2000). Electroosmosis was first investigated by researchers in geophysical sciences, who found water migration through porous clay diaphragms under an applied electric field (*Reuss*, 1809). With the rapid development of microfluidic in the past few years, electroosmosis has drawn a wide attention due to its pressure-building ability. Extensive theoretical and experimental works on electroosmosis have been reported to further the physical understanding and realize the most advanced application of this basic phenomenon.

After a broad review of the currently available literature on the electrokinetic transport combining the mechanisms of electroosmotic flow and capillary electrophoresis, it can be concluded that most of the studies done so far in this area assume negligible effects of Joule heating on the electrokinetic transport. However, it is well known that Joule heating is resulted from inevitable volumetric heating when an electric field is applied across conducting media such as electrolyte. In general, such heat is rejected through the capillary wall and the downstream end of the capillary to the surrounding, and it would lead to an increase of buffer temperature and develop temperature gradients along both radial and axial directions inside the buffer solution. The elevation of buffer temperature and the induced temperature gradient would in turn affect the electroosmotic flow and capillary electrophoretic transport by influencing the temperature sensitive buffer and sample properties such as viscosity, dielectric constant, electric conductivity, diffusivity, electromobility, and pH value. In the application of capillary electrophoretic separation, the negative consequences associated with the Joule heating phenomena include sample band dispersion or peak broadening, and thus low column separation efficiency and reduction of analysis resolution. Further, significant temperature rise may lead to the

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decomposition of thermally labile samples and even the formation of vapor bubbles (*Knox and McCormack*, 1994a). In addition, under a constant voltage operation mode, the positive feedback between temperature and electric conductivity of buffer solutions would cause the so-called “auto-thermal effect”, and hence it imposes limitations for the performance of capillary electrophoresis (*Lynch and Saville*, 1981). On the other hand, some potential applications of the Joule heating and Joule heating induced temperature gradient in microfluidic devices were recently reported (*Ross et al.*, 2002, *De Mello et al.*, 2004). Therefore it is important to deepen our understanding of the thermal aspects of electrokinetic transport so as to achieve a better design and process control of the capillary electrophoresis. Nonetheless, the reported studies on Joule heating and its effects on the electrokinetic transport are limited. And majority of them are merely experimental investigation with simple extensions of the basic theory. The analyses reported in the literature are based on simplified theories and/or empirical correlations, and those theoretical models did not consider the full coupling among the electric field, flow field and temperature field. To address the Joule heating associated coupled problem, computer-aided numerical simulation is needed to solve these coupled fields. To the best of the author’s knowledge, there is still no study reported on the Joule heating effects on the electrokinetic sample transport based on the rigorous mathematical models, and there is still much scope to explore the thermal aspects of electrokinetic transport in microchannel networks.

Thus this study serves as an attempt to fulfill the present void by carrying out a fundamental, systematic and in-depth exploration on the Joule heating and its effects on the electrokinetic sample transport in microfluidic systems.

1.2 Objectives

To minimize the Joule heating and its effects on the separation efficiency, the strategy adopted by researchers is to use the trial-and-error method to choose and control parameters such as the applied electric field, capillary inner dimension, buffer ionic concentration, and/or active temperature control, etc. No scientific guidance or standards on the basis of rigorous mathematical models are available in the literatures. In practice, various cooling modes such as use of liquid coolant in well-thermostated systems or air by natural/forced convection in non-thermostated systems have been developed to maintain a proper capillary temperature and thus minimize the Joule heating effects. In addition, motivated by the low cost, many microfluidic systems are made from the polymer material, which causes quite different Joule heating effects from that of the glass based microfluidic systems. Therefore the main objective of this thesis is to investigate the Joule heating and its effects on the electrokinetic transport in different microfluidic systems with different operation parameters, and aims to increase the understanding of the thermal aspects of the electrokinetic transport so as to achieve a better design and process control of the capillary electrophoresis. In summary, the objectives of this thesis are highlighted in the following:

- (1) To develop comprehensive mathematical models describing the Joule heating and its effects on the electroosmotic flow and sample species electrokinetic transport by investigating the physical phenomena of the electro-kinetic transport in the microfluidic systems,
- (2) To perform numerical investigation on Joule heating and its effects on the electrokinetic transport in the cylindrical microchannels in a commercial capillary electrophoresis system with thermo-stated cooling system. This can be

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achieved by conducting systematic, quantitative studies of the effects of the applied electric field, capillary inner dimension, buffer ionic concentration, and temperature control mode.

- (3) To perform the 3D numerical investigation of Joule heating and its effects on the electrokinetic transport in the rectangular microchannels in a microfluidic system with natural air convection cooling mode. This can be achieved by conducting systematic, quantitative studies of the effects of the Joule number, channel thickness, and channel wall material.
- (4) To fabricate microchannels, set up an experimental test rig and carry out experiments to verify the proposed mathematical model and the numerical code. Extensive experimental data under a wide variety of hydrodynamic and physicochemical conditions will be accumulated.

Although majority of this study is theoretical in nature, the information uncovered by the modeling and experimental results can be of great importance to the development, optimization and control of the microfluidic systems.

1.3 Outline of the dissertation

There are eight chapters in this dissertation. Chapter 1 serves as an introduction to the background and motivation of this work. The latest development and application of microfluidics and the importance of Joule heating and its effects are presented. The objectives of this project are then outlined. In the end, the literature of existing studies on the electroosmotic flow, capillary electrophoresis, Joule heating and its effect in microchannels is thoroughly reviewed and remarked.

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In chapter 2, the theory of electric double layer (EDL) is presented at first, and then the mathematical models describing the Joule heating and its effects on the electroosmotic flow and sample species electrokinetic transport are developed.

In chapter 3, the numerical method employed in this project is presented in detail. The grid systems and Power-law scheme are first introduced, then the Revised Semi-Implicit Method for Pressure Linked Equations (SIMPLER) method for solving the pressure-related items in the incompressible Navier-Stokes equation and the solver for solving discrete algebraic equation are presented. Finally, the Crank-Nicolson scheme is introduced to compare with the power-law scheme.

In Chapter 4, the numerical code is validated by comparing the simulation result with the analytical solution. Motivated by the fact that no study was reported to validate the widely used Boltzmann distribution (versus the general Nernst-Planck equation), two different mathematical models (i.e. the ionic concentration distributions are governed by either the Nernst-Planck equation or the Boltzmann distribution) describing the electroosmotic flow in the developing region and fully developed region with Joule heating effects are solved. The differences of ionic concentration distributions, electrical double layer potential profiles, velocity and temperature fields obtained by solving these two different models are then quantitatively compared. Finally, the proper model is suggested for studying in the Joule heating and its effects.

Chapter 5 presents the Joule heating and its effects on the electrokinetic transport in the cylindrical microchannels in the commercial capillary electrophoresis system with thermo-sated cooling mode. Transient temperature development and electroosmotic flow velocity are discussed at first, and then a thorough parametric

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study of the Joule heating and its effects on electroosmotic flow and sample species transport is carried out.

Chapter 6 presents the Joule heating and its effects on the electrokinetic transport in the rectangular microchannels in the microfluidic systems with natural convection cooling mode. Then a systematic study of the Joule heating and its effects on electrokinetic transport is carried out and the effects of various parameters are presented.

In chapter 7, experimental studies are presented. The microchannels are fabricated using the soft lithography technique, and an experimental test rig is set up. Experiments are carried out and the experimental results are compared with the numerical simulation results.

Finally, Chapter 8 provides major results and findings from this research work. The contributions are highlighted and some possible directions for further studies are briefly outlined.

1.4 Literature review

Electrokinetic transport phenomena (i.e. electroosmosis, electrophoresis etc.) have found a variety of practical applications, including the dewatering of soils, removing of mine tailings and waste sludge, and removing contaminants from soils (*Hunter*, 1981). During recent years, due to the rapid development of the microfluidics based BioMEMS (or Biochip) technology, the electroosmosis has been exploited as a basic mechanism to transport and control liquid samples of nanovolumes in microdevices used for chemical and biological analysis and medical diagnosis (*Bousse et al.*, 2000). In the literature, numerous theoretical studies have

been reported on the electrokinetic flow in fine capillaries of various geometric cross sections.

1.4.1 Steady electrokinetic flow in microchannels

1.4.1.1 Analytical studies

According to *Pamukcu* (1997), the electrokinetic phenomenon was first observed by *Reuss* in 1809. When a DC current was applied to a clay-water mixture, water moved through the capillary towards the cathode under the electric field. When the electric potential was removed, the flow of water immediately stopped. *Napier* (1846) distinguished electroosmosis from electrolysis. In 1861, *Quincke* found the electric potential difference through a membrane resulted from streaming potential.

Helmholtz first treated electroosmotic phenomena analytically in 1879. The basic model for electroosmosis is attributed to *Smoluchowski* in 1921 on the consequences of applying pressure and potential gradients across capillaries filled with an electrolyte. Out of this treatise of the subject the well-known Helmholtz-Smoluchowski (H-S) theory was developed (*Hiemenz*, 1986). The H-S theory deals with electroosmotic & electrophoretic velocity of a fluid of certain viscosity and dielectric constant through a surface-charged porous medium of zeta potential (ζ), under an electric potential gradient. The formulation of the problem is based on the assumption of large electrokinetic diameter; the contribution due to the EDL thickness is neglected. Despite that his classical results for the EOF plug velocity and streaming potential are still frequently employed during routine experimental works on the EOF.

Burgreen and *Nakache* (1964) formulated a mathematical model for the electroosmotic flow in an ultrafine slit. *Rice* and *Whitehead* (1965) calculated analytically the correction factors that must be applied to the Smoluchowski's results

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when dealing with narrow capillaries having arbitrary electrokinetic diameters. However the Rice and Whitehead theory itself is subject to the severe restriction that the zeta potential be sufficiently low to permit the Debye-Hückel approximation, effectively limiting the application of their predictions in $\zeta \leq 25$ mV for a 1-1 electrolyte.

Levine et al. (1975) extended the Rice and Whitehead model to high zeta-potentials for the electrokinetic flow in cylindrical capillaries. They developed an analytical approximation to solve the Poisson-Boltzmann equation within the capillary, in a fashion similar to the method used by *Philip and Wooding* (1970) who solved this equation outside a charged cylindrical particle immersed in an electrolyte. And it was shown that Philip and Wooding yielded results which differed only slightly from those by numerical method.

Keh and Liu (1995) analytically studied the steady EOF in a long uniform circular capillary bearing a solvent-permeable and ion-penetrable layer of adsorbed poly-electrolytes on its inside wall. They obtained the electrical potential and space charge density distributions by solving the linearized P-B equation. Their results on the EOF demonstrate that the structure of the surface charge layer can result in an augmented or diminished EOF relative to that in a capillary with bear walls, depending on the characteristics of the electrolyte solution, surface charge layer, and capillary.

Mala et al. (1997) investigated the interfacial electrokinetic effects on characteristics of liquid flow and heat transfer between two parallel plates. Experiments were conducted to study the effect of the EDL on flow characteristics with different ionic concentrations and plate materials. The Debye-Hückel linear approximation was used in the formulation of the electrical potential distributions and

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a mathematical model was developed for a steady-state liquid flow with the consideration of the EDL effects.

Qian et al. (1997) proposed a numerical algorithm to obtain the electrical potential distributions in a charged capillary filled with general electrolytes by introducing the Poisson-Boltzmann (P-B) integral equation. The algorithm removes the difficulty caused by steep variation of the potential near the wall of the capillary. They also extended their studies to evaluate the accuracy of numerical solutions of the nonlinear Poisson-Boltzmann equation for charged colloidal particles (*Qian et al.*, 1998). An assessment method was developed to show it is valid not only for arbitrary surface potentials and also for complex geometry.

The electrokinetic flows in rectangular microchannels has been studied by *Yang et al.* (1997, 1998, 2002a) since in practice the cross-section of microchannels made by modern micromachining technology is in practice close to a rectangular shape. In these works, both steady state and transient fully developed, laminar liquid flow in rectangular microchannels were studied. The two-dimensional nonlinear Poisson-Boltzmann (P-B) equation governing the EDL was numerically solved using a finite-difference scheme. An exact solution for the velocity of EOF was obtained by solving the modified N-S equation using the Green function method. The bulk temperature distributions were also achieved by solving the energy equation for rectangular microchannel using the control – volume based finite difference method.

Cummings et al. (2000) examined the conditions for similitude between the fluid velocity and electric field in electroosmotic flow. They highlighted the difficulty of generating computation meshes to numerically simulate electroosmotic flow. The mathematical equations governing electroosmotic flows must be resolved in length

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scales ranging from a Debye layer thickness of perhaps 10 nm, to channel widths on the order of 100 μm and to device lengths of nearly 10 cm.

Arulanandam and Li (2000a), and *Yang and Huang* (2001) investigated the influence of interfacial electrokinetic phenomena in rectangular microchannels. In their studies a two dimensional electrokinetic model was proposed to account for the “corner effect”. Based on the Debye-Hückel approximation, a linear solution of two-dimensional P-B equation was presented to describe the EDL potential distributions in the cross-section of rectangular channels. An exact solution for the EOF velocity was obtained by employing the Green function formulation.

Qu and Li (2000) proposed a model to determine the electrical potential and ionic concentration distributions in overlapped EDL fields. Two infinitely large plates were considered. It was found that using the classical theory to evaluate the potential distributions in an overlapped EDL region would lead to an inaccurate description due to the misuse of the Boltzmann equation and the boundary conditions. Hence they derived a new set of governing equations for the overlapped EDL fields without using the Boltzmann equation.

Tsao (2000) studied the electroosmosis flow through an annulus under the Debye-Hückel linear approximation and the velocity profile was obtained by using the Stokes equation. He introduced a geometry-dependent correction factor to the electroosmotic mobility described by the Helmholtz–Smoluchowski equation.

Kang et al. (2002a) extended Tsao’s model to study the electroosmotic flow in a capillary annulus with high zeta potentials. Earlier, Tsao studied the electroosmotic flow through an annulus under the Debye-Hückel linear approximation, indicating that work is limited to low zeta potentials ($\zeta \leq 25\text{mV}$). Therefore, an analytical scheme was proposed to solve the nonlinear Poisson-Boltzmann (P-B) equation in an

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annulus domain. It was shown that the EDL effect is more significant in small-sized annuluses since the EDL potential extends to a larger portion of the annulus when the electrokinetic diameter, κa is small. The calculations showed that when the two walls of an annulus are oppositely charged, there exists a plane of zero velocity where the liquid flows in opposite direction when it passes through this plane.

Ren and Li (2001) and *Gleeson* (2001, 2002) investigated the characteristics of the EOF in a cylindrical microchannel with non-uniform zeta potential. Their theoretical and numerical results showed the distorted electroosmotic velocity profiles resulting from the axial variation of the zeta potential. Also, the influences of the unequal section size and the direction of the zeta potential change on the velocity profile, the induced pressure distributions, and the volumetric flow rate were discussed. The simulation results reveal possible effects of bio-adhesion in microchannels on the electroosmotic flow in biochip devices.

Hsu et al. (2002) studied the electrokinetic flow of an electrolyte solution through an elliptical microchannel theoretically. The elliptical cross-section of the microchannel is chosen as it can simulate various geometries by adjusting its shape parameters.

Recently, under the thin electric double layer approximation (which is valid for electrokinetic flow in most microfluidic channels), *Zholkovskij et al.* (2003) formulated an analytical expression for solute dispersion in microchannels having different cross sections for arbitrary zeta potentials and symmetric/non-symmetric electrolytes.

1.4.1.2 Numerical simulation studies

In numerical studies, *Patankar* and *Hu* (1998) developed a three-dimensional numerical scheme to simulate steady-state electroosmotic flows in complicated geometry. The injection of the sample solution in a cross-channel device for capillary electrophoresis was studied. Diffusion and Joule heating are neglected in the formulation of the numerical method. Their results reasonably agree with the experiment done by *Fan* and *Harrison* (1994).

Ermakov et al. (1998) presented the mathematical models describing the electrokinetic flow and sample manipulation in microchips. Two fundamental microfluidic chip elements, a cross and a mixing tee, are of particular interest. Three mass transport mechanisms including convection, electrophoretic transport and diffusion were considered and the sample concentration was assumed small as compared to the concentration of the buffer solution. The buffer solution concentration was assumed to be large enough such that the EDL layer thickness on the channel walls could be neglected when compared to the channel dimensions. The simulation results were compared with experimental data. Good agreement between simulated results and experimental data suggests the accuracy of their proposed mathematical models.

Hu et al. (1999) presented a numerical study for steady electrokinetic flow in intersecting channels in a T-shaped configuration. The nonlinear Poisson-Boltzmann equation was solved numerically by employing the finite difference method. The modified Navier-Stokes equations and the continuity equation were solved numerically by employing the SIMPLER algorithm (*Patankar*, 1991).

Samson and Marchand (1999) developed a numerical model to study the drift of ions in an electrolyte solution when a chemical potential gradient is present. The

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numerical model developed is able to calculate the concentration and potential profiles for very complex transport phenomenon and the chemical activity is taken into consideration. Numerical simulations were performed for two cases: low and high concentration levels. The Debye-Hückel model is valid only for low concentration levels not higher than 10 mmol/l. A one-dimensional problem was presented and the numerical model can be easily extended to a two-dimensional problem when the chemical activity coefficient is taken into account.

Griffiths et al. (2000) employed analytical and numerical methods to study the electroosmotic flow in a tube and a channel when the zeta potential is not small. The results showed that the normalized mean fluid speeds of the tube and the channel show the same trend but the normalized mean fluid speeds of the channel is everywhere higher than that of the tube.

Bianchi et al. (2000) studied electroosmotic flow at a T-junction by using finite element simulation. Their results indicated that relative zeta potential and channel width are two predominant parameters affecting the distributions of flow at the intersection. *Mitchell et al.* (2000) simulated a steady-state electroosmotic flow in three different geometries by using meshless analysis based on Finite Cloud Method (FCM). Their results show that linear approximation of Poisson-Boltzmann equation for large zeta potentials can predict the plug velocity accurately but fails to predict the velocity variation close to the walls.

Erickson and Li (2002) studied the effects of surface electrokinetic heterogeneity on the electroosmotic flow and mixing efficiency of a T-shaped micromixer through 3D numerical simulations. While all cases of surface heterogeneity were shown to enhance species mixing, they found that the greatest improvements can be achieved when the zeta potential of the heterogeneous surface is

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of opposite sign to that of the homogeneous surface, resulting in localized circulation zones within the bulk flow field.

Recently, *Fu et al.* (2003a) use the Nernst–Planck model to numerically explore the effect on the EOF in the case where the EDL overlaps within the channel. In addition, the capillary electrophoretic transport is used extensively to control buffer flow and manipulate samples of nano/pico-liter volumes (Ren, et al., 2003, Ng, et al., 2004). By utilizing the numerical simulation approach, *Tsai et al.* (2005) investigate the electrokinetic transport processes and the control parameters in the injection systems with a variety of different configurations including the cross-form, T-form, double-T form etc.

1.4.1.3 Experimental studies

Koh and Anderson (1975) experimentally investigated the electroosmotic flow in charged microcapillaries of ellipse shape. They compared the data with numerical calculations and showed that adsorption of the potential determining ions is dependent on electrostatic potential at the pore wall.

Coufal et al. (1994) investigated several factors affecting the magnitude and reproducibility of the electroosmotic flow in silica capillary tubes. These are the nature of the buffer, the presence of additives inside the capillary tubes, the manufacturing conditions, and the pretreatment of the capillary. The results showed that the nature of the running buffer significantly affects the repeatability and the magnitude of the electroosmotic mobility. The column manufacturing process and its pretreatment are less important factors.

Herr et al. (2000) presented an analytical and experimental study of electroosmotic flow (EOF) in cylindrical capillaries with non-uniform zeta potential

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distributions. The experiment focuses on examining electroosmotic flow under a uniform applied field in capillaries with an EOF-suppressing polymer adsorbed onto various fractions of the total capillary length. This fractional EOF suppression was achieved by coupling capillaries with different zeta potentials. A newly developed caged-fluorescence technique was utilized to extract information about the fluid velocity profiles and sample dispersion rates.

In view of the fact that electroosmotic flow is mainly used for delivering and separating chemical and biological samples, various studies on the sample transport, separation and injection have been reported. *Harrison et al.* (1992) examined and demonstrated the feasibility of using electroosmotic pumping to control flow and separate samples in a manifold of flow channels without the use of valves. A complex manifold of capillary channels was fabricated in a planar glass substrate. In their paper, the μ -TAS concept was explored where the technique was to couple capillary electrophoresis (CE), a powerful separation method, together with flow injection analysis (FIA) on a planar substrate. The effectiveness of the glass substrate for electrophoretic separation was compared with the conventional fused-silica capillaries.

Dasgupta et al. (1994) demonstrated experimentally that an EOF pump is able to replace conventional pumping devices in established flow-injection analysis (FIA) systems. They showed that although there is the disadvantage of EOF pump against backpressure, it could be overcome by selecting appropriate conduit diameters. By introducing a membrane joint between the carrier holding coil and the sample injection valve, electrostacking can also be performed.

Tassel et al. (1996) presented a new method of controlling protein adsorption onto the surface of fused silica capillary during capillary electrophoresis (CE). It

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involves the placement of a thermally treated, irreversibly adsorbed layer of fibrinogen onto the internal surface of a fused silica capillary. The stability of the adsorbed layer was investigated by applying an electric field to the buffer solution in two separate capillaries, each coated with fibrinogen but with only one receiving thermal treatment. Their findings provide further investigations on the effectiveness of protein-coated capillaries in CE separations.

Yeung et al. (1997) explored several approaches for suppressing the electroosmotic flow and minimizing wall adsorption. In their work, the use of low ionic concentrations of zwitterionic surfactants to suppress the electroosmotic flow and prevent the adsorption of cationic proteins on the walls of the capillary were investigated. By adding zwitterionic surfactants to an electrophoretic buffer, it suppresses the electroosmotic flow by 50% - 90%. Three zwitterionic surfactants were prepared and their effects on suppressing electroosmotic flow at various pH conditions were compared and discussed.

Culbertson et al. (2000) demonstrated a new microchip functional element that is capable of electrokinetically inducing a pressure differential along the length of a channel for hydraulic pumping. This functional element consists of a tee intersection with one inlet channel and two outlet channels. The inlet channel is maintained at high voltage and one outlet channel is connected to ground and the other channel has no electric potential applied. The pump is shown to differentially transport ions down the two outlet channels. It can also separate cations and neutrals from anions by changing the flow resistance in the field-free channel relative to the ground channel. This differential transport and separation of ions provide unique solutions to biochemical analysis problems that require a continuous separation of cations from anions.

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Lab-on-a-chip devices usually involve replacing one solution with another in a microchannel by electroosmotic pumping. *Ren et al.* (2001) presented both the theoretical and experimental studies of electroosmotic flow in a capillary with one electrolyte solution displacing another solution. A theoretical model was developed to predict the electroosmotic flow displacing and mixing processes. The experiment involved applying an electrical field under a constant voltage to simulate the displacing process. Base on this study, *Ren et al.* (2002) proposed a new method to determine the average electroosmotic velocity for the solution-replacing process flow in microchannels by using the slope of the measured current-time relationship. To determine the reliability of this method, a numerical method was also developed to calculate the average velocity in a microchannel with one solution displacing another solution. The results showed a good agreement between the model predictions and the experimental results.

Werner et al. (1998) developed an experimental setup to study the electrokinetic potential and the surface conductivity of flat surfaces. The new device accommodates the variability of the distances between two parallel flat sample surfaces forming a slit channel. Different aqueous electrolyte solutions were used. The zeta potential was calculated at different channel geometries and the surface conductivity was determined from the extrapolation of the channel conductance values gained at a number of sufficiently small distances.

Arulanandam and Li (2000b) provided an experimental procedure for determining the zeta potential and surface conductance by monitoring the electrical current in electroosmotic flow through a capillary. A known method of measuring the average velocity based on current monitoring in electroosmotic flow was used to evaluate zeta potential ζ . The surface conductance, λ_s can also be determined based

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on the current measurements. Knowing λ_s , the relative contributions of the surface conductance and the bulk fluid conductivity to the measured total current can be determined. From the experiments, it was found that the average velocity was independent of capillary size but dependent on the electrolyte concentration and the applied field.

Erickson et al. (2000) developed an improved method to determine the zeta potential ζ and surface conductance λ_s by employing the slope-intercept method. In the classical slope-intercept method of obtaining ζ and λ_s , it neglected the electrokinetic effects on the liquid flow. With the improved slope-intercept method, the following three conditions are met: large channels, thin EDL and sufficiently small streaming potential such that electroosmotic body force on the mobile ions can be ignored. Both the classical and improved slope-intercept methods were applied to experimental streaming potential data.

Fu et al. (2003b) presented an experimental and numerical investigation into electrokinetic focusing injection on microfluidic chips. In addition, several new techniques for the sample species focusing and stacking in capillary electrophoresis systems have been developed by *Jung et al.* (2003), *Herr et al.* (2003) and *Balss et al.* (2004), and thousand folds of sample concentration or signal were obtained.

1.4.2 Transient electrokinetic flow in microchannels

1.4.2.1 Analytical studies

López-García et al. (2000) studied the dynamics of EDL in both time and frequency domains, and provided insights into the transient behavior of potential, velocity, and ion concentration profiles. They analyzed how potential and ion

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concentration profiles, particle or fluid velocity evolve in the nanosecond to microsecond time range after the application of an electric field. A network method was proposed to gain information about the evolution with time of the potential, counter-ion, and co-ion perturbations, the particle velocity, and the fluid velocity profile.

Santiago (2001) studied the effects of fluid inertial and pressure on the transient velocity and vorticity fields of electroosmotic flow in a two-dimensional microchannel. His work is based on the classical Debye-Hückel linear approximation in solving P-B equation to obtain the electric double layer potential distributions and a validated slip velocity condition proposed by *Overbeek* (1952). In typical on-chip electrokinetics applications, the flow field can be separated into an inner flow region dominated by viscous and electrostatic forces and an outer flow region dominated by inertial and pressure forces. These two regions are separated by a slip velocity condition determined by the Helmholtz-Smoluchowski equation. The validity of this slip velocity condition was investigated by analyzing the velocity field in a two-dimensional flow channel with an impulsively started electric field. The regime for which the inner/outer flow model is valid was described in terms of non-dimensional parameters.

Without assumption of thin double layer thickness, *Keh* and *Tseng* (2001) analytically studied the transient response of electrolyte solutions in a narrow capillary tube and slit to a step change in the applied electric field and pressure gradient by solving the linearized P-B equation. The modified Navier-Stokes equation was solved analytically to obtain the electrical potential and transient velocity profiles. Their results demonstrated that the behavior of the transient electrokinetic flow in a capillary tube and in a capillary slit is similar; however, the rate of evolution

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of the flow in a tube with time is faster by a factor of about 2 than that in a slit with its half thickness equal to the tube radius.

In recent years, the use of time dependent electric fields has proved another practical and useful technique in maneuvering the electroosmotic flow. For instance, *Söderman and Jönsson* (1996) developed a theoretical framework for the description of the time and spatial resolution of electroosmosis for both planar and cylindrical geometries under the effect of pulsed electric fields. Specifically, sinusoidally alternating (AC) electric fields are more often applied to investigate the frequency dependent nature of the fluid velocity or the motion of the nano-particles, whose mechanism in the literature is termed as *AC* electroosmosis (*Ramos et al.*, 1999). It offers advantages over scanning-probe methods of nano-particle manipulation in that the equipment used is simple, cheap and has no moving parts, relying entirely on the interactions between the particle and dynamic electric field.

In a study on electrokinetic instability micromixing, *Oddy et al.* (2001) developed an electrokinetic process to rapidly stir micro-and nano liter volume solutions for microfluidics bioanalytical applications. They obtained the electroosmotic velocity profile in a micromixer by using slip velocity approximation, in which the velocity on the outskirts of the flow field is bounded by the “slip velocity”.

Yang et al. (2002b) studied the transient analysis of electroosmotic flow in a slit microchannel. Exact solutions for the electrical potential profile and the transient electroosmotic flow field were obtained by solving the complete Poisson–Boltzmann equation and the Navier-Stokes equation under an analytical approximation for the hyperbolic sine function. The results showed that between the analytical scheme

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proposed in their work and the complete numerical scheme were visually indistinguishable, indicating excellent approximation of the analytical scheme.

Kang et al. (2002b) presented an in-depth analysis of the dynamics of electroosmotic flow in a cylindrical microcapillary. A time-dependent electric field was applied to the transient electroosmotic flow field. In addition, the flow field excited by a sinusoidal ac field was also discussed. The complete Poisson-Boltzmann equation was analytically solved and exact solutions for the transient velocity distributions and the time-dependent mean velocities were obtained using the Green's function formulation.

Analytical solutions for the time-dependent neutral solute dispersion were obtained by solving the transient diffusion-convection equation in transformed spatial and temporal coordinates for both low and high zeta potentials (*Griffiths and Nilson*, 1999, 2000). In addition, *Marcos et al.* (2004) presented an analysis of the frequency- and time-dependent electroosmotic flow in a closed-end rectangular microchannel. An exact solution to the modified Navier–Stokes equation governing the AC electroosmotic flow field was obtained by using the Green's function formulation in combination with a complex variable approach. An analytical expression for the induced backpressure gradient was derived.

1.4.2.2 Numerical simulation studies

Yang et al. (2001a) investigated the time and space development for the entry region of an electroosmotic flow through a microchannel between two parallel plates by numerically solving the combination of the Poisson, Nernst-Planck, and full Navier-Stokes equations. They also unified the applied electrical potential and the zeta potential instead of the superposition method previously employed. They

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discussed the effects of the entrance region on the fluid velocity distributions, charge density boundary layer, entrance length, and shear stress. They found the entrance length of the electroosmotic flow is longer than that of the classical pressure-driven flow. The thickness of the electrical double layer (EDL) in the entry region is thinner than that in the fully developed region. The change of velocity profile is more pronounced in the entrance region. The velocity profile across the channel height is in a parabolic shape at the entry point, and changes to a flat shape stage by stage as it moves to the fully developed region when the Reynolds number is small. While the velocity profile will change to a concave shape in the fully developed region when the Reynolds number is large.

1.4.2.3 Experimental studies

In general, an electrokinetic process takes place when pressure gradients or voltage differences are established between two liquid subsystems in contact through a membrane or a porous medium. So far, in the study of electrokinetic processes, static electric fields are used to obtain a direct current (DC) circulating the membrane system. In the recent years, the use of time-dependence electric fields have been shown useful for studying certain membrane aspects such as the alternating current (AC) spectroscopy technique. It has been found out that the capacitance and conductance of the membrane system depend on the frequency of the ac field. Thus, the presence of an AC perturbation may influence the electrokinetic phenomena. *Barragán and Bauzá (2000)* performed electroosmosis experiments through a cation-exchange membrane, and showed that the presence of AC perturbation affects the electroosmotic flow value, depending on the frequency of AC signal and the solution stirring conditions. In the frequency range studied, two regions have been observed

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where the electroosmotic flow reaches a maximum value: one at low frequencies ($10^{-1} - 10^1$ Hz); the other at frequencies of the order of $10^2 - 10^5$ Hz. These regions could be related to membrane relaxation phenomena.

Recently, the instability of the electrokinetic microchannel flow was theoretically and experimentally studied by *Lin et al.* (2004) and *Oddy and Santiago* (2005). By using the electrokinetic instability, *Shin et al.* (2005) obtained the enhanced mixing in microchannels. In addition, an experimental and numerical investigation of electrokinetic micromixing was carried out by *Fu et al.* (2005) and the rapid double-T-form microfluidic mixer was designed.

1.4.3 Joule heating and its effects

1.4.3.1 Analytical studies

However, all aforementioned studies assume a negligible effect of Joule heating on electroosmotic flow. It is well known that the so-called Joule heating is generated when an electric field is applied across conductive liquids. Such Joule heating not only can cause temperature increase but also may create temperature gradient. The change of liquid temperature and the presence of temperature gradient would have an impact on the electroosmotic flow and bio-sample transport and separation. Previous studies have demonstrated that the effects of Joule heating can result in low column separation efficiency, reduction of analysis resolution, and even loss of injected samples. In addition, temperature rise can lead to the decomposition of thermally labile samples and the formation of gas bubbles as well. On the other hand, one can also take advantage of the Joule heating effects to precisely control the buffer temperature in microfluidic devices as demonstrated by Caliper (*Caliper*, CA, USA)

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scientists, and to develop a new technology – microfluidics temperature gradient focusing as reported by *Ross and Locascio* (2002).

Studies of the Joule heating and its effects on EOF and sample separation have been reported using theoretical and experimental approaches. Simplified theoretical analyses and empirical methods were conducted to obtain analytical expressions for the effect of the Joule heating on buffer mean temperature, electroosmotic velocity and electrophoretic mobility. The Joule heating induced thermal effects on the band spreading in capillary electrophoresis were analyzed by considering the temperature-dependent buffer viscosity on the basis of the bulk temperature elevation (*Knox*, 1988) and the radial temperature profile under both natural and forced convection (*Knox and McCormack*, 1994b).

Based on a parabolic temperature profile assumption, *Grushka et al.* (1989) examined the effect of radial temperature gradients on the efficiency of capillary zone electrophoretic separation and proposed certain conditions for operating the capillary electrophoretic system to minimize the undesirable effects of thermal gradients. The results showed that temperature gradient in capillary electrophoresis, resulting from the passage of current, could have serious effects on the efficiency of the system.

At the same time, as the assumption of parabolic radial temperature profiles was questionable by several other researchers, *Jones et al.* (1989) studied the effect of temperature differences on the efficiency of capillary zone electrophoresis. A simplified 1D expression for the radial temperature profile in capillary zone electrophoresis was derived in this study, taking into account the temperature dependence of the buffer electrical conductivity and the polyimide coating of the quartz capillary, and hence their model can address the “autothermal effect” and shows more close to experimental data when compared to the constant-conductivity

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model. The results showed that in typical capillary zone electrophoresis experiments with low power inputs, the temperature profile rigorously derived is nearly identical to a parabolic profile, and at high input powers, the parabolic approximation underestimates the temperature at the capillary center. Moreover, they proposed a novel approach to compensate the thermal band broadening effect by imposing an opposite small Poiseuille flow.

Zhang et al. (2001) and *Cross et al.* (2001) discussed the models and methods used to calculate joule heating in capillary zone electrophoresis. Their discussions showed that the temperature increase due to Joule heating is quite significant for high buffer concentrations.

EL-Hakim (2000) analytically studied the effects of viscous dissipation, thermal dispersion and joule heating on magnetohydrodynamic (MHD) free convection flow with a variable plate temperature in a micropolar fluid in the presence of uniform transverse magnetic field.

Boland et al. (2001) investigated the temperature and velocity profiles for free convection flows in cylindrical pores when a homogeneous heat source was presented. The mean temperature of the pore domain was obtained by using the condition of total energy conservation in the system. They found that the temperature profile is of a parabolic shape. The results presented in this study are useful to study the process of mixing in capillary electrophoresis.

Based on the assumption of constant thermophysical properties, the characteristics of Joule heating induced thermal convection in EOF (*Maynes and Webb*, 2003a, 2004, *Horiuchi and Dutta*, 2004) and a combined EOF and pressure-driven flow (*Maynes and Webb*, 2003b) were analytically examined using classic idealized thermal boundary conditions.

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Recently, analytical solutions for the effects of Joule heating on sample band broadening were obtained by *Xuan and Li* (2004a, 2005a, 2005b) and *Wang et al.* (2004).

1.4.3.2 Experimental studies

Many experimental and synthetic studies of Joule heating in capillary electrophoresis have been reported. *Gobie et al.* (1990) analytically and experimentally studied the thermal band broadening in capillary electrophoresis and proposed an improved thermal model for estimating the Joule heating induced band broadening. The result showed that the auto-thermal effect made CE capillaries run significantly hotter than what the constant electric conductivity models predict. In this study, a method to reduce the capillary electrophoresis band broadening due to joule heating by imposing a small opposing Poiseuille flow was proposed.

Chidambara and Hunter (1991) assessed the temperature increase due to joule heating in the capillary by solving the energy equation, and they also measured the temperature distributions in different buffer solutions. In their study, the importance of auto-thermal effect was addressed. *Knox and McCormack* (1994a, 1994b) had demonstrated three independent methods for calculating the temperature in the capillary using the experimental results they obtained.

Lukkari et al. (1994) developed an in-house built temperature control unit for a commercial capillary electrophoresis apparatus. With this inexpensive and simple temperature control unit, the separation temperature was effectively controlled. The separate efficiency was greatly increased and the electroosmotic flow rates were remarkably improved.

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Kelly Swinney (2002) for the first time measured the extent of Joule heating in chip-scale capillary electrophoresis (CE) by using of a novel picoliter volume interferometer. The experimentally obtained temperature increment was compared with the theory. It was found the temperature changes were similar to those predicted for capillary of equivalent dimensions. The results indicate that the true operating temperature must be taken into account in order to optimize separation in capillary electrophoresis systems.

Xuan et al. (2004b) use fluorescence-based techniques to measure the liquid temperature variation and the electroosmotic velocity profile along a microchannel. Their experimental results were found to agree well with the predictions of the numerical model.

1.4.3.3 Numerical simulation studies

Although many analytical and experimental studies focused on the Joule heating and its effects in the capillary electrophoresis, the theoretical models developed by the aforementioned studies did not consider the full coupling among the electric field, flow field and temperature field. To address the Joule heating associated coupled problem, computer-aided numerical simulation is needed to solve these coupled fields. However, only few numerical studies on the Joule heating effect on the electroosmotic flow, electrophoresis and sample separation have been reported.

Bosse and Arce (2000) carried out systematic studies of Joule heating effect on dispersive mixing in electrophoretic cells, focusing on both hydrodynamic and convective-diffusive transport aspects. However, their analysis is only limited to electrophoretic cells where the two ends of the cell are closed. Furthermore, their models did not include electroosmotic flow.

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Zhao and Liao (2002) presented a model, which coupled the Poisson-Boltzmann equation, Navier-Stokes equation, and energy equation. The model was solved numerically to study the behavior of EOF under a non-isothermal condition. Motivated by rapid development of PDMS-based microfluidic devices, *Erickson et al.* (2003) presented a finite-element model to analyze Joule heating and its heat transfer in a PDMS microfluidic system. *Xuan et al.* (2004c) numerically investigated the thermal end effects on the electroosmotic flow in a microchannel. Their model includes the coupling electric field strength which is subject to local change due to the non-uniform electric conductivity. However, Joule heating effects on the electrophoretic mass transport has not been addressed in these numerical studies.

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MATHEMATICAL MODELS

2.1 Introduction

In recent years, electrokinetic mass transport has been investigated theoretically and experimentally. *Harrison et al.* (1992) integrated a capillary electrophoresis and sample injection system on a planar glass chip. *Seiler et al.* (1993) improved the instrumentation and experimental method for the device described by *Harrison et al.* (1992). *Harrison et al.* (1993) performed electroosmotic pumping and electrophoretic separation of samples using a device consisting of two intersecting channels micromachined in silicon. Most successful theoretical studies of sample electrokinetic transport have been conducted using computer modeling which was initiated by *Bier's* group (1983). Computer modeling has been used to simulate capillary electrophoresis (CE) by *Ermakov et al.* (1994, 1995a, 1995b, 1998a) and *Thormann et al.* (1998).

Most models are limited to 1-D cases. There are a few reports which solved 2-D and 3-D problems, such as modeling of electrokinetically driven mass transport phenomena in microfabricated chip devices (*Ermakov et al.*, 1998b). Electroosmotic flow in a rectangular channel intersection has been studied using 3D flow simulations by *Patankar and Hu* (1998).

However, all aforementioned studies assume a negligible effect of Joule heating on electrokinetic mass transport. So far, no rigorous mathematical models have been formulated to describe the Joule heating and its effects on the electrokinetic mass transport in microfluidic devices. This chapter therefore attempts to develop a comprehensive mathematical model to study the Joule heating effects in microfluidic devices.

2.2 Electrical double layer potential

Fig. 2-1 shows the schematic diagram of the structure of the *electric double layer* (EDL) and the electrical potential profile near a charged surface (*Probstein, 1994*). Most surfaces obtain a certain amount of surface charges when they are in contact with a polar medium. Such surface charges, in turn, influence the distributions of nearby ions in the polar medium. Opposite charge ions (i.e., counter-ions) to that of surface are attracted towards the surface while like charge ions (i.e., co-ions) are repelled from the surface. This electrostatic interaction, combined with the combined tendency resulting from the random thermal motion of the ions, leads to the formation of an *electric double layer* (EDL). Generally, the EDL can be divided into an inner, compact layer and an outer, diffuse layer. The compact layer, which is also called the Stern layer, contains a layer of counter-ions that are strongly attracted to the surface and are immobile. The thickness (δ) of the stern layer is about several Angstroms, and it is separated from the diffuse layer by the *Stern plane*. Ions whose centers are located beyond the Stern plane form the diffuse mobile part of the double layer.

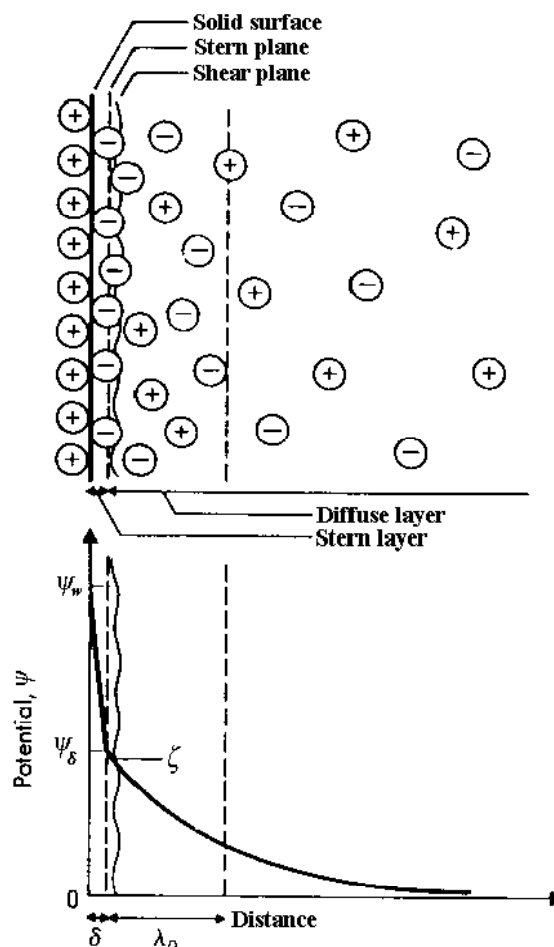


Fig. 2-1 Schematic diagram of an electric double layer (EDL) and the electrical potential profile near a charged surface, including the solid surface where the electrical potential is ψ_w , the stern plane where the potential is ψ_δ , and the shear plane where the potential is ζ (Probstein, 1994).

The thickness of the diffuse layer generally ranges from several to a few hundreds of nanometers (λ_D), depending upon the bulk ionic concentration and other properties of liquid. The electrical potential changes from the surface potential, ψ_w to the Stern plane potential, ψ_δ within the Stern layer, and decays to zero at the bulk phase far away from the Stern plane. The potential at the Stern plane, ψ_δ is close to the *electrokinetic*

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potential or *zeta potential*, ζ , which is defined as the potential at the shear surface between the charged surface and the electrolyte solution. ζ is measurable from experiments, and it also characterizes the strength of the EDL. It is a determining factor for the ionic distributions in the diffuse layer.

According to the theory of electrostatics, the displacement vector ($\vec{D}$) of the ions in an electrically polarized solution can be written as (Probstein, 1994)

$$\nabla \cdot \vec{D} = \rho_e \quad (2-1)$$

where ρ_e is the net charge density. The displacement vector is related to the electric field vector and the electric polarization vector by (Probstein, 1994)

$$\vec{D} = \varepsilon_0 \vec{E}_\psi + \vec{P}_o \quad (2-2)$$

where, ε_0 , $\vec{E}_\psi$ and $\vec{P}_o$ are the permittivity of vacuum, the electric field vector due to the electrical double layer potential, and the electric polarization vector, respectively. For a linear material, the polarization vector $\vec{P}_o$ is proportional to the electric field strength through (Masliyah, 1994)

$$\vec{P}_o = \chi \varepsilon_0 \vec{E}_\psi \quad (2-3)$$

where χ is the electric susceptibility of the electrolyte. It is related to the dielectric constant $\varepsilon(T)$ of the electrolyte solution given by

$$\varepsilon(T) = 1 + \chi \quad (2-4)$$

The dielectric constant of the electrolyte solution here is considered as a function of temperature. Eq. (2-1) then becomes

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$$\nabla \cdot [\varepsilon(T) \vec{E}_\psi] = \frac{\rho_e}{\varepsilon_0} \quad (2-5)$$

Note that

$$\vec{E}_\psi = -\nabla \psi \quad (2-6)$$

Here, ψ is the electrical potential distribution. Substituting Eq. (2-6) into Eq. (2-5) leads to

$$\nabla \cdot [\varepsilon(T) \nabla \psi] = -\frac{\rho_e}{\varepsilon_0} \quad (2-7)$$

Eq. (2-7) is the Poisson's equation relating the spatial variation in the electric field to the charge distribution (*van de Ven*, 1989). In Eq. (2-7), the net charge density is given by

$$\rho_e = \sum_{i=1}^N n_i \sigma_i e \quad (2-8)$$

where n_i is the ionic number concentration of the i -th species. σ_i is the valence of the i -th ion species, e is the magnitude of charge on an electron (fundamental charge), and N is the number of ionic species in the electrolyte solution.

Combining Eq. (2-7) and (2-8) leads to

$$\nabla \cdot [\varepsilon(T) \nabla \psi] = -\frac{\sum_{i=1}^N n_i \sigma_i e}{\varepsilon_0} \quad (2-9)$$

For a simple fully dissociated symmetrical electrolytes, i.e. $\sigma_+ = \sigma_- = \sigma$, the local net charge density becomes

$$\rho_e = \sigma e (n_+ - n_-) \quad (2-10)$$

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where n_+ and n_- are the ionic number concentration of the cations and anions, respectively. Then the equation governing electrical potential distributions can be simplified to

$$\nabla \cdot [\varepsilon(T) \nabla \psi] = -\frac{\sigma e(n_+ - n_-)}{\varepsilon_0} \quad (2-11)$$

2.3 Externally applied electric potential

Since the electroosmotic flow is driven by an externally applied electric field, the applied electric field distribution needs to be formulated. When an external electric potential is applied, current flows through the electrolyte, the conservation of charges can be written as (Masliyah, 1994)

$$\frac{\partial \rho_e}{\partial t} = -\nabla \cdot \vec{I}_t \quad (2-12)$$

where $\vec{I}_t$ and t are the electric current density and time, respectively. The electric current is a result of the motion of all the ionic species in the electrolyte solution, it consists of the contributions from diffusion current $\vec{I}_d$, electromigration current $\vec{I}_e$, and convection current $\vec{I}_c$, which can be expressed as (Masliyah, 1994)

$$\vec{I}_t = \vec{I}_d + \vec{I}_e + \vec{I}_c \quad (2-13)$$

where,

$$\vec{I}_c = \rho_e \vec{u} \quad (2-14)$$

$$\vec{I}_d = -e \sum D_i(T) \sigma_i \nabla n_i \quad (2-15)$$

$$\vec{I}_e = -\frac{e^2 \nabla \phi}{k_b T} \sum \sigma_i^2 D_i(T) n_i = -\lambda(T) \nabla \phi \quad (2-16)$$

where $\vec{u}$ is the velocity vector of the bulk fluid, $D_i(T)$ is the diffusion coefficient of the i th ionic species, T is the absolute temperature, k_b is the Boltzmann constant, $\lambda(T) = -\frac{e^2}{kT} \sum \sigma_i^2 D_i(T) n_i$, is temperature dependent electrical conductivity of the electrolyte solution, and ϕ is the externally applied electric potential.

Generally, the diffuse double layer is very thin when compared with the size of the channel, and the net charge density outside the EDL can be considered as zero. Then by neglecting the EDL effect on the externally applied electric field, the electrolyte solution in the entire channel can be regarded as electrically neutral, i.e. $\rho_e = 0$. This assumption will generally hold except in those instances where the EDL thickness is large as compared with the channel size. Further, when there is no concentration gradient, in other words, no diffusion current occurs in the electrolyte solution. With these assumptions, Eq. (2-12) can be written as

$$-\nabla \cdot I_t = \nabla \cdot [\lambda(T) \nabla \phi] = 0 \quad (2-17)$$

In this thesis, Eq. (2-17) is referred as the modified Laplace equation governing the distribution of the externally applied electric potential of ϕ .

2.4 Electroosmotic flow field

The EOF arises when the mobile portion of the diffuse double layer interacts with an external electric field in the regime near the charged surface. Based on the abovementioned EDL theory, there is evidently no charge neutrality within the double layer since the number of counter-ions is more than the number of co-ions. In other

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words, the counter-ions predominate and the local net charge density is not zero within the EDL. If an external electric field is applied tangentially along a charged surface, the electric field will exert a coulombic force on the ions in the diffuse layer. The migration of the mobile ions will carry the adjacent liquid with them, leading to an EOF. Due to viscous forces, the flow is carried through beyond the EDL region to the rest of the liquid in the microchannels. This electrokinetic phenomenon was first investigated by *Reuss* (1809), who demonstrated that under the influence of an applied electric field water migrated through porous clay diaphragms towards the cathode. When a DC current was applied to the clay-water mixture, water moved through the capillary towards the cathode under the electric field. When the electric potential was removed, the flow of water immediately stopped. This fact can be well understood today in that the clay, sand and other mineral particles usually carry negative surface charges when in contact with water; the water normally contains small quantities of dissociated salts. As described above, electroosmotic flow is induced through the micropores in the clay, upon application of electric field.

Generally, for a viscous Newtonian fluid of uniform and homogeneous composition, conservation of momentum as expressed through Newton's second law applied to a fluid control volume can be written as (*Probstein*, 1994)

$$\rho \frac{D\vec{u}}{Dt} = \vec{F}_s + \vec{F}_b \quad (2-18)$$

where the operator $\frac{D(\)}{Dt} = \frac{\partial(\)}{\partial t} + (\vec{u} \cdot \nabla)(\)$ is called substantial derivative, which is applied to all parameters depending on both time and position. ρ , $\vec{u}$, $\vec{F}_s$ and $\vec{F}_b$ are the solution density, velocity, total surface forces and total body forces, respectively.

In most typical microfluidic systems, the buoyancy effect can be neglected (i.e.,

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neglecting the gravitational body force) as compared to the forced convection (refer to Appendix A). For the convectional pressure-driven incompressible flow, the total surface and body forces can be expressed as (*Probstein, 1994*)

$$\vec{F}_b = 0 \quad (2-19)$$

$$\vec{F}_s = -\nabla p + \nabla \cdot [\mu(T) \nabla \vec{u}] \quad (2-20)$$

where, p and $\mu(T)$ are the pressure, and temperature-dependent viscosity respectively.

Combining Eqs. (2-18), (2-19) and (2-20), leads to

$$\rho \frac{D\vec{u}}{Dt} = -\nabla p + \nabla \cdot [\mu(T) \nabla \vec{u}] \quad (2-21)$$

This is the general Navier-Stokes equation for the pressure-driven incompressible flow.

Different from the conventional pressure-driven flows, the driving force of the electroosmotic flow is due to the interaction between net charge density in the EDL regime and the applied electric field. Neglecting the electrostriction due to the change of the dielectric constant and the gravitational body force, the driving force of the electroosmotic flow can be written as (*Eringen and Maugin, 1990*)

$$\vec{F}_b = \rho_e \vec{E} \quad (2-22)$$

Recognizing that the electric field strength $\vec{E}$ is related to the externally applied electric potential ϕ given by

$$\vec{E} = -\nabla \phi \quad (2-23)$$

Therefore, the Navier-Stokes equations including the continuity and momentum equations describing a laminar, incompressible flow of an electrolyte solution with temperature-dependent viscosity are modified to the following form (*Probstein, 1994*)

$$\rho \frac{D\vec{u}}{Dt} = -\nabla p + \nabla \cdot [\mu(T)\nabla\vec{u}] - \rho_e \nabla \phi \quad (2-24)$$

For the incompressible fluid, the conservation of mass requires that

$$\nabla \cdot \vec{u} = 0 \quad (2-25)$$

Equation (2-25) is referred to as the Continuity equation.

2.5 Joule heating induced temperature field

The Joule heating induced temperature field is governed by the energy equation and the energy equation taking into account of temperature-dependent thermal conductivity and heat source can be expressed as

$$\rho c_p \frac{DT}{Dt} = \nabla \cdot [k_l(T)\nabla T] + S \quad (2-26)$$

where c_p and $k_l(T)$ are the specific heat, and thermal conductivity of the liquid solution.

S is the heat source term. The heat source term can be further expressed as the sum of the viscous dissipation (Φ_{th}) and the Joule heating ($\dot{q}$), given by

$$S = \Phi_{th} + \dot{q} \quad (2-27)$$

In general microfluidic system with small velocity gradients, the viscous dissipation (Φ_{th}) can be neglected as compared with Joule heating. The Joule heating term ($\dot{q}$) can be expressed as

$$\dot{q} = \frac{I_t^2}{\lambda(T)} \quad (2-28)$$

Substituting Eq. (2-13) and Eq. (2-16) into Eq. (2-28), the Joule heating term can be further expressed as

$$\dot{q} = \lambda(T) |\vec{E} \cdot \vec{E}| = \lambda(T) |\nabla \phi \cdot \nabla \phi| \quad (2-29)$$

Therefore the energy equation considering the Joule heating effect can be written as

$$\rho c_p \frac{DT}{Dt} = \nabla \cdot [k(T) \nabla T] + \lambda(T) |\nabla \phi \cdot \nabla \phi| \quad (2-30)$$

2.6 Ionic concentration distributions

The ionic concentration distributions, in general, are governed by the Nernst-Planck equation. While in most cases, the Boltzmann distribution is employed to describe the ionic concentration distributions because of its simplicity. In this study, the ionic concentration distributions are assumed to follow these two different models; one is the Nernst-Planck equation; and the other is the Boltzmann distribution.

2.6.1 Nernst-Planck equation

In general, the ionic concentration distribution n_i is described by the Nernst-Planck equation (*van de Ven*, 1989), and it can be expressed as,

$$\frac{Dn_i}{Dt} = \nabla \cdot [D_i(T) \nabla n_i] + \nabla \cdot \left[\frac{n_i \sigma_i e D_i(T)}{k_b T} \nabla (\psi + \phi) \right] \quad (2-31)$$

2.6.2 Boltzmann distribution

For simplicity, the ionic concentration distributions in a symmetric electrolyte may also be assumed to follow the Boltzmann distribution (*Yang et al*, 1998).

$$n_+ = n_0 \exp\left(-\frac{\sigma e \psi}{k_b T}\right) \quad n_- = n_0 \exp\left(\frac{\sigma e \psi}{k_b T}\right) \quad (2-32)$$

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where n_0 is the bulk ionic number concentration in the electrolyte solution. Under this special case, the local net charge density for a simple fully dissociated symmetrical electrolyte becomes

$$\begin{aligned} \rho_e &= \sigma e (n_+ - n_-) = \\ n_0 \sigma e \left[\exp\left(-\frac{\sigma e \psi}{k_b T}\right) - \exp\left(\frac{\sigma e \psi}{k_b T}\right) \right] &= -2n_0 \sigma e \sinh\left(\frac{\sigma e \psi}{k_b T}\right) \end{aligned} \quad (2-33)$$

Hence the Poisson Equation can be written as

$$\nabla \cdot (\varepsilon(T) \nabla \psi) = \frac{2n_0 \sigma e}{\varepsilon_0} \sinh\left(\frac{\sigma e \psi}{k_b T}\right) \quad (2-34)$$

Eq. (2-36) is normally referred to as the Poisson-Boltzmann equation governing the charge distribution for a symmetric electric solution (e.g. NaCl, KCl, or NaHCO₃)

2.7 Mass species transport equation

Up to this point, the closure governing equations describing the Joule heating and its effects on electroosmotic flow in a microcapillary have been presented. Since electroosmotic flows are often used for injection and separation of biological or chemical samples such as the separation of DNA in genetic engineering, another objective of this research is to study the role of Joule heating in the sample species transport.

Consider a sample species to transport from one reservoir to the other reservoir through the capillary that is filled with an electrolyte solution (see Fig. 2-2).

For the purpose of analysis, assumptions are made for no adsorption of sample species onto the capillary wall and no interaction between sample species and the electrolyte solution components. As the species transported by electrokinetic means in

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general is accomplished by three mechanisms including convection, diffusion, and electrophoresis, the mass transport equation can be formulated as (Masliyah, 1994)

$$\frac{DC_s}{Dt} = \nabla \cdot [D_s(T) \nabla C_s] \quad (2-35)$$

where C_s is the sample species concentration and $D_s(T)$ is the temperature-dependent mass diffusivity of the sample species.

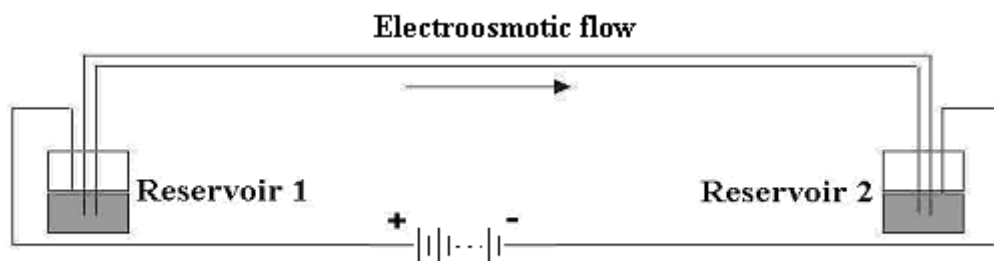


Fig. 2-2 Schematic diagram of the sample species transport.

2.8 Summary

In this chapter, the mathematical models describing the phenomena of the EOF and electrokinetic mass transport with Joule heating effects were formulated.

The models developed in this study include the Poisson equation governing the EDL potential distribution, the modified Laplace equation governing the externally applied electric potential distribution, the modified Navier-Stokes (N-S) equation describing the motion of liquid driven by electrokinetic body forces, and the energy equation governing the temperature field due to Joule heating. In addition, two different ways of modeling the ionic concentration distribution are considered in this project, i.e., using the Nernst-Planck (N-P) equation or the Boltzmann distribution. Since the

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electrical and thermophysical properties including the dielectric constant in the Poisson equation, the electrical conductivity in the Laplace equation, the liquid viscosity in the N-S equations and the energy equation, the electrical conductivity in the energy equation, the ionic mass diffusion coefficient in the N-P equation are considered to be temperature dependent. The Poisson equation, the N-S equations, the energy equation, and the N-P equation (or Boltzmann distribution) are strongly coupled. Hence the governing equations will be solved simultaneously using the CFD technique. Moreover, in view of the fact that electroosmotic flow is mainly used for delivering and separating chemical or biological samples, the mass species transport equation is therefore added into the model development to examine the Joule heating effect.

CHAPTER 3 NUMERICAL METHOD

3.1 Introduction

In this chapter, the numerical method used for solving the proposed mathematic models is described. The numerical scheme is developed based on the finite volume method (FVM) developed by *Patankar* (1980). The governing equations derived in chapter 2 are discretized using the control volume integration method, and the staggered grid system is utilized. To deal with the pressure-related equations, the electroosmotic flow field is obtained by solving the equations using the Revised Semi-Implicit Method for Pressure Linked Equations (SIMPLER).

3.2 The general form of the governing equations

In general, all the governing equations derived earlier including the Poisson equation, the Laplace equation, the Navier-Stokes equation, the energy equation, the Nernst-Planck / Boltzmann equations and the mass transport equation can be classified as a convection–diffusion equation. According to *Patankar* (1980), the general form of the convection-diffusion equation can be expressed as

$$\underbrace{\frac{\partial(\rho\Phi)}{\partial t}}_{Transient} + \underbrace{\frac{\partial(\rho U_j \Phi)}{\partial x_j}}_{Convection} = \underbrace{\frac{\partial}{\partial x_j} \left(\Gamma \frac{\partial \Phi}{\partial x_j} \right)}_{Diffusion} + \underbrace{S}_{Source} \quad (3-1)$$

where Φ denotes the dependent variable, Γ is the diffusion coefficient, and S is the source term. It is an important step that all the relevant differential equations such as the Poisson equation, the Laplace equation, the Navier-Stokes equation, the energy equation, the mass transport equation and other related phenomena can be considered

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as special cases of the general convection-diffusion Φ equation. As a consequence, a general illustration of numerical schemes and solutions will be centered on the convection-diffusion equation, i.e. Eq. (3-1).

3.3 Discretization

The numerical solution of a differential equation consists of a set of numbers from which the distributions of the dependent variable Φ can be constructed. The unknown values of the dependent variable are defined at a finite number of locations (grid points) in the calculation domain. The continuous information, contained in the exact solution of the differential equation, is replaced with discrete values at the grid points. This replacement process is referred to as discretization.

There are several ways of deriving the discretization equations, such as the Taylor series approach, the variational formulation, the method of weighted residuals and the control-volume formulation. In this study, the control volume formulation is used.

3.3.1 Finite volume method (FVM)

In the FVM, the conservation principles are applied to a fixed region in space known as a control volume (CV). The domain is divided into a number of control volumes such that there is one control volume surrounding each grid point. The grid point is located at the center of a control volume. The governing equation is integrated over each control volume and its surface to obtain an algebraic equation (Eq. (3-2)) containing the grid point values of Φ .

$$\oint_A J \cdot n dA + \iiint_{\Omega} S d\Omega = 0 \quad (3-2)$$

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where the first term represents the total fluxes (J) through the surface (A) of the control volume, and the second term represents the source term in the control volume (Ω). The discretization equation then expresses the conservation principle for a finite control volume just as the partial differential equation expresses it for an infinitesimal control volume. The resulting solution implies that the integral conservation of quantities such as mass, momentum, and energy is exactly satisfied for any group of control volumes and of course, for the whole domain.

3.3.2 Discretized equation

The grid systems used to discretize the general equation is discussed in Appendix B. To derive the discretized equation, a typical three-dimensional control volume (taken from Fig. A-1) with a unite thickness is presented in Fig. 3-1. The CV interface is subdivided into four plane faces, denoted by lower case letters corresponding to their direction (e , w , n and s) with respect to the central node P . The nodes are denoted by upper case letters E , W , N , and S .

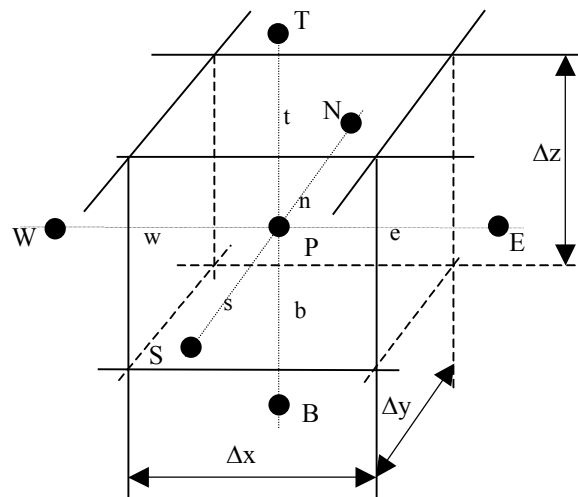


Fig. 3-1 A typical control volume and the notation used for a Cartesian 3D grid.

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Using the method developed by *Patankar* (1980), the general governing equation Eq. (3-1) can be discretized as:

$$a_P \Phi_P = a_E \Phi_E + a_W \Phi_W + a_N \Phi_N + a_S \Phi_S + a_T \Phi_T + a_B \Phi_B + a_P^0 \Phi_P^0 + b \quad (3-3)$$

where

$$a_E = D_e A(|P_e|) + \|-F_e, 0\| \quad (3-4a)$$

$$a_W = D_w A(|P_w|) + \|F_w, 0\| \quad (3-4b)$$

$$a_N = D_n A(|P_n|) + \|-F_n, 0\| \quad (3-4c)$$

$$a_S = D_s A(|P_s|) + \|F_s, 0\| \quad (3-4d)$$

$$a_T = D_t A(|P_t|) + \|-F_t, 0\| \quad (3-4e)$$

$$a_B = D_b A(|P_b|) + \|F_b, 0\| \quad (3-4f)$$

$$a_P = a_E + a_W + a_N + a_S + a_T + a_B - S_P \Delta V \quad (3-4g)$$

$$b = S_C \Delta V \quad (3-4h)$$

$$a_P^0 = \frac{\rho \Delta V}{\Delta t} \quad (3-4i)$$

$$\Delta V = \Delta x \Delta y \Delta z \quad (3-4j)$$

The flow rates and diffusion rates are defined as:

$$F_e = (\rho u)_e \Delta y \Delta z \quad D_e = \frac{\Gamma_e \Delta y \Delta z}{(\delta x)_e} \quad (3-5a)$$

$$F_w = (\rho u)_w \Delta y \Delta z \quad D_w = \frac{\Gamma_w \Delta y \Delta z}{(\delta x)_w} \quad (3-5b)$$

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$$F_n = (\rho u)_n \Delta x \Delta z \quad D_n = \frac{\Gamma_n \Delta x \Delta z}{(\delta y)_n} \quad (3-5c)$$

$$F_s = (\rho u)_s \Delta x \Delta z \quad D_s = \frac{\Gamma_s \Delta x \Delta z}{(\delta y)_s} \quad (3-5d)$$

$$F_t = (\rho u)_t \Delta y \Delta x \quad D_t = \frac{\Gamma_t \Delta y \Delta x}{(\delta x)_t} \quad (3-5e)$$

$$F_b = (\rho u)_b \Delta y \Delta x \quad D_b = \frac{\Gamma_b \Delta y \Delta x}{(\delta x)_b} \quad (3-5f)$$

where ΔV is the volume of the CV, and Δt is the time step. $\Delta x, \Delta y, \Delta z$ are the distances between control volume interfaces. $\delta x, \delta y, \delta z$ are the distances between grid points. F_e, F_w, F_n, F_s, F_t , and F_b are the flow rates through the control volume interfaces. S_C and S_P are coefficients for source terms, and Γ is the harmonic mean of two grid points. For the unsteady term, the “old” value is denoted by superscript 0. In conformity with the fully implicit practice, all other values (i.e. those without a superscript) are to be regarded as the “new” value. The power-law formulation is

$$A(|P|) = \left\| 0, (1 - 0.1|P|)^5 \right\| \quad (3-6)$$

where P is Peclet number, $\|A, B\|$ is defined as the greater of A and B .

The Eq. (3-3) is derived by using a 3D Cartesian coordinate system. However, the same format of the discretization equation can be obtained in any orthogonal coordinate systems such as the cylindrical coordinated system. Only the definitions of F , D and ΔV are different, and they are provided in Table 3-1.

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Table 3-1 Definitions of terms in different coordinate systems

Coordinate System Terms	Cartesian (3D)	Cartesian (2D)	Cylindrical (Axis-symmetric)
F_e	$(\rho u)_e \Delta y \Delta z$	$(\rho u)_e \Delta y$	$(\rho u)_e r \Delta r$
F_w	$(\rho u)_w \Delta y \Delta z$	$(\rho u)_w \Delta y$	$(\rho u)_w r \Delta r$
F_n	$(\rho u)_n \Delta x \Delta z$	$(\rho u)_n \Delta x$	$(\rho u)_n r \Delta x$
F_s	$(\rho u)_s \Delta x \Delta z$	$(\rho u)_s \Delta x$	$(\rho u)_s r \Delta x$
F_t	$(\rho u)_t \Delta y \Delta x$	-	-
F_b	$(\rho u)_b \Delta y \Delta x$	-	-
D_e	$\frac{\Gamma_e \Delta y \Delta z}{(\delta x)_e}$	$\frac{\Gamma_e \Delta y}{(\delta x)_e}$	$\frac{\Gamma_e r \Delta r}{(\delta x)_e}$
D_w	$\frac{\Gamma_w \Delta y \Delta z}{(\delta x)_w}$	$\frac{\Gamma_w \Delta y}{(\delta x)_w}$	$\frac{\Gamma_w r \Delta r}{(\delta x)_w}$
D_n	$\frac{\Gamma_n \Delta x \Delta z}{(\delta y)_n}$	$\frac{\Gamma_n r \Delta x}{(\delta x)_n}$	$\frac{\Gamma_n \Delta x}{(\delta x)_n}$
D_s	$\frac{\Gamma_s \Delta x \Delta z}{(\delta y)_s}$	$\frac{\Gamma_s r \Delta x}{(\delta x)_s}$	$\frac{\Gamma_s \Delta x}{(\delta x)_s}$
D_t	$\frac{\Gamma_t \Delta y \Delta x}{(\delta z)_t}$	-	-
D_b	$\frac{\Gamma_b \Delta y \Delta x}{(\delta z)_b}$	-	-
ΔV	$\Delta x \Delta y \Delta z$	$\Delta x \Delta y$	$r \Delta x \Delta r$

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The procedure for discretizing the general convection-diffusion equation in the presence of flow field is formulated in the above section. However, except in some very special circumstances, it is not possible to specify the flow field. Rather, we must calculate the local velocity components from the corresponding governing equations. The velocity components are governed by the momentum equations, which are the special case of the general differential equations for Φ (i.e. Eq. (3-1)). The pressure gradient forms a part of the source term in the momentum equation. In the staggered grid system described in Appendix B, the discretized momentum equations are similar to the discretized general equations. If the pressure field is given, the discretized x -momentum equation can be expressed as

$$a_w u_w = \sum a_{nb} u_{nb} + b + (p_w - p_p) A_w \quad (3-7)$$

In Eq. (3-7), $A_w = \Delta y \Delta z$ and a_{nb} are the coefficients of the adjacent points. The momentum source term is b . The definitions of these coefficients are the same as those provided in the previous section. It should be mentioned here that the calculation of the diffusion coefficients and mass flow rates at the u velocity CV interface usually requires an appropriate interpolation.

However, there is no existing equation for describing pressure, and the pressure field is indirectly specified via the continuity equation. Therefore, in the momentum equations, the pressure source term needs a special treatment, and should be separated from the source term. In this study, the pressure-velocity coupling momentum equations are solved using the Revised Semi-Implicit Method for Pressure Linked Equations (SIMPLER) (see Appendix C).

3.4 Underrelaxation for nonlinear problems

The coefficients of the discretized equations may be a function of the dependant variable. For example, in energy equation, the thermal conductivity may depend on temperature, and in momentum equation, the mass flow rates are dependant on velocity. So the discretized equations are nonlinear in nature. The iterative method therefore is needed to solve these nonlinear equations. First, the coefficients in the discretized equations are calculated using guessed values of the dependant variable. Then, the linearized algebraic equations are solved to obtain updated values. Next, the coefficients are recalculated using the new updated values, and the equations are solved again. This process is repeated until the convergent results are obtained.

In order to avoid divergence during iterative process, a change of variable in each iteration steps should be reduced gradually. This process is called underrelaxation. The underrelaxation method is presented as follows.

On the n th iteration, the algebraic equation for general variable Φ_p can be written as

$$a_p \Phi_p^n = \sum a_{nb} \Phi_{nb}^n + b \quad (3-8)$$

Then

$$\Phi_p^n = \frac{\sum a_{nb} \Phi_{nb}^n + b}{a_p} \quad (3-9)$$

An underrelaxation method can be expressed as

$$\Phi_p^n = \Phi_p^{n-1} + \alpha(\Phi_p^n - \Phi_p^{n-1}) \quad (3-10)$$

where $0 < \alpha \leq 1$.

Substituting Eq. (3-8) into Eq. (3-10) gives

$$\frac{a_P}{\alpha} \Phi_P^n = \sum a_{nb} \Phi_{nb}^n + b + (1 - \alpha) \frac{a_P}{\alpha} \Phi_P^{n-1} \quad (3-11)$$

The optimum value of the underrelaxation factor α varies from case to case. Underrelaxation can be applied to parameters in the equation, such as viscosity, density etc.

3.5 Boundary conditions

The algebraic equation relates the variable value at the center of a CV to the values at several neighbor CVs. If the boundary conditions are given, the numbers of equations and unknowns are equal to the number of CVs. So the algebraic equations can be solved coordinately.

The boundary conditions can be given as the following different types:

1. Boundary values are given;
2. Boundary fluxes are given; and
3. Boundary fluxes are provided as a combination of a reference value and boundary data.

Different types of boundary conditions can be treated in different ways. A brief discussion is provided as follows.

For the first type of boundary condition, the boundary values are given, and no additional formulation is needed.

For the second type of boundary condition (i.e. the given boundary fluxes), the boundary conditions can enter into the discretized equations by suppression of the link to boundary side and modification of the source terms. The appropriate coefficient of

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the discretized equation is set to zero, and the boundary side flux is introduced through the source term S_C and S_P . This method is discussed below.

For example, in energy equation, if the heat flux is given (see Fig. 3-2 (a))

$$S_{extra} = \frac{q_B(\text{area})}{\text{volume}}, \quad S_{C,extra} = S_{extra}, \quad S_{P,extra} = 0 \quad (3-12)$$

For the third type of boundary condition, that means the heat transfer coefficient h and fluid temperature T_f are given (see Fig. 3-2 (b))

$$q_B = \frac{T_f - T_B}{1/h} = \frac{T_B - T_P}{\delta/\Gamma} = \frac{T_f - T_P}{\frac{1}{h} + \frac{\delta}{\Gamma}} \quad (3-13)$$

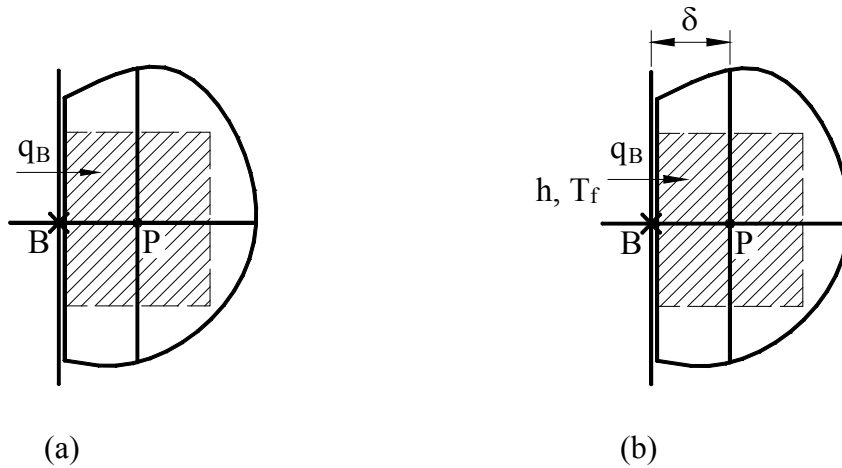


Fig. 3-2 Boundary conditions.

Then,

$$S_{extra} = \frac{q_B(\text{area})}{\text{volume}} = \frac{T_f - T_P}{\frac{1}{h} + \frac{\delta}{\Gamma}} \frac{(\text{area})}{(\text{volume})} \quad (3-14)$$

$$S_{C,extra} = \frac{T_f}{\frac{1}{h} + \frac{\delta}{\Gamma}} \frac{(\text{area})}{(\text{volume})}, \quad S_{P,extra} = \frac{-1}{\frac{1}{h} + \frac{\delta}{\Gamma}} \frac{(\text{area})}{(\text{volume})} \quad (3-15)$$

3.6 Convergence criteria

When using the iterative method (Appendix D) to solve linear algebraic equations or nonlinear problems, it is important to know where the iteration stops. The most common practice is based on the difference between two successive iterations. The iteration is stopped when the difference is less than a pre-selected value. Some of these convergence criteria are listed below.

For velocity, the maximum residual and the sum of the residual can be used as convergence criteria. From Eq. (B-9),

$$R_{\max} = \left| (\rho_w u_w^* - \rho_e u_e^*) \Delta y + (\rho_s u_s^* - \rho_n u_n^*) \Delta x \right|_{\max} \quad (3-16)$$

$$R_{\text{sum}} = \sum \left[(\rho_w u_w^* - \rho_e u_e^*) \Delta y + (\rho_s u_s^* - \rho_n u_n^*) \Delta x \right] \quad (3-17)$$

For scalar variable, the difference between two successive iterations can be considered as a convergence criterion,

$$\left| \frac{\Phi^n - \Phi^{n-1}}{\Phi^n} \right|_{\max} \leq \varepsilon \quad (3-18)$$

$$\left| \Phi^n - \Phi^{n-1} \right|_{\max} \leq \varepsilon \quad (3-19)$$

3.7 Crank-Nicolson scheme for mass transport equation

As mentioned in previous sections, the equations describing the electrokinetic phenomena are generally typical convection-diffusion equations (i.e. Eq. (3-1)). Numerically solving these typical convection-diffusion equations has attracted a large amount of attention due to the many challenges it offers, especially for the special mass species transport equation (Eq. (2-37)). Since in general cases concerned in Biochip operations, because of the very low diffusion coefficient of sample species

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(e.g., $D_0 \approx 10^{-10} \text{ m}^2/\text{s}$), it generally gives a large Peclet number. For this kind of special mass species transport problem, the convection is dominant, i. e.

$$\|\vec{U}(X)\| \gg \|\Gamma(X)\| \quad (3-20)$$

where the X denotes the general coordinate of the control volume (i.e. x, y, z), the aforementioned power law scheme reduces to the first order accuracy and gives rise to higher numerical pseudo diffusion, resulting in unrealistic mass species transport results.

Various numerical methods, having reasonable accuracy and stability properties, have been suggested to overcome difficulties arising in the simulation of such kind of convection dominated diffusion flows. Among them, the Crank-Nicolson method has been employed and studied in this project.

The Crank-Nicolson method, using the average variable value at current time ($t+1$) and previous time (t), is a semi-implicit scheme of second order accuracy in both time and space, and is expressed by (*Crank and Nicolson, 1997*)

$$\frac{\Phi_X^{t+1} - \Phi_X^t}{\Delta t} + \frac{1}{2}\Omega[\Phi_X^{t+1} + \Phi_X^t] = S_X^{t+1/2}, \quad \Omega = \Omega_c + \Omega_d \quad (3-21)$$

where Ω denotes the second-order (central) approximations for the convection (Ω_c) and diffusion (Ω_d) operators. In general, Eq.(3-21) equivalently reads

$$\left(1 + \frac{\Delta t}{2}\Omega\right)\Phi_X^{t+1} = \left(1 - \frac{\Delta t}{2}\Omega\right)\Phi_X^t + \Delta t S_X^{t+1/2} \quad (3-22)$$

3.8 Summary

The numerical method used to solve the general convection-diffusion equation is described. The grid systems, the numerical schemes, the Revised Semi-Implicit Method for Pressure Linked Equations (SIMPLER) method for solving the pressure-related items in the incompressible Navier-Stokes equation, and the solver for solving discrete algebraic equation are presented in detail. Specifically, for the convection-dominant convection-diffusion equation (i.e. refers to the mass transport equation in this project), the Power law scheme itself reduces to first order accuracy, and induces higher numerical pseudo diffusion. Combining with the first order implicit scheme (in time), it was classified as the first order scheme for the mass transport equation in this project. In addition, the Crank-Nicolson scheme, which includes the semi-implicit scheme for the temporal discretization and central difference (CD) scheme for the spatial discretization, i.e. a scheme of second order accuracy in both time and space, is introduced to compare with the power-law scheme.

CHAPTER 4

VALIDATION OF BOLTZMANN DISTRIBUTION

4.1 Introduction

As mentioned in chapter 1, due to the rapid development of Lab-on-a-chip (or Biochip) technology, the EOF is extensively used as a transporting mode to manipulate liquids such as pumping, valving, mixing, splitting and delivering solute samples of nanovolumes in microfluidics devices. In the literature, a great deal of information has been generated on the EOF in microcapillaries. While we have noticed that because of its simplicity, the Boltzmann distribution is assumed to describe the ionic concentration distributions in their studies by most of those researchers. Strictly speaking, the Boltzmann distribution is applicable only when the system is in thermodynamic equilibrium (*Masliyah*, 1994). If there exists a liquid flow, the ionic concentration distributions may be affected by the presence of the fluid motion (*Yang, et al.*, 1998b). Furthermore, since the mass diffusivity of ions can be temperature dependent, the presence of temperature gradient resulting from the Joule heating may also cause the ionic concentration distributions to deviate from the Boltzmann distribution. Therefore, the general Nernst–Planck equation should be used to describe the ionic concentration distributions in these situations. However, in the literature, no study has been reported to quantitatively compare the ionic concentration distributions obtained from these two models. A systematic study is therefore carried out to evaluate the ionic concentration distributions in both the developing and the fully developed *EOF* regions on the basis of the Nernst-Planck equation and the Boltzmann distribution.

In this chapter, mathematical models for the *EOF* in cylindrical capillaries with Joule heating effects are presented. Specifically, the ionic concentration distributions

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are modeled using (i) the general Nernst-Planck equation to account for the influence of the fluid flow and the temperature field, and (ii) the simple Boltzmann distribution. All relevant equations are coupled through temperature-dependant parameters, such as the electrolyte dielectric constant, liquid viscosity, ion diffusion coefficient, and thermal and electric conductivities etc. These coupled equations are numerically solved and a comparison has been made for the results of the ionic concentration distributions, electrical potential distributions, and the *EOF* and temperature fields obtained from the Nernst-Planck equation and the Boltzmann distribution. In addition, the computational domain in the present chapter and in Chapter 5 is chosen as a cylindrical microcapillary, which is widely used in several bioengineering processes such as capillary electrophoresis (CE) and high-performance liquid chromatography (HPLC) (*Heineman et al*, 2001 and *Harrison et al*, 1993).

4.2 Governing equations

The model presented in this chapter includes the Poisson equation governing the *EDL* potential distributions, the Laplace equation governing the externally applied electric field distributions, the modified Navier-Stokes equation describing the motion of liquid driven by electrokinetic body forces, and the energy equation governing the temperature field due to Joule heating. The ionic concentration distributions are either governed by the Nernst-Planck equation or described by the Boltzmann distribution. Therefore, two sets of equations are formulated to describe the electrokinetic transport phenomenon in a microchannel with consideration of the Joule heating effect.

Consider an electroosmotic flow in a cylindrical microcapillary of an inner radius, R and a length, L as shown in Fig. 4-1.

In such a cylindrical coordinate system, the governing equations can be written as:

4.2.1 Poisson's equation

$$\frac{1}{r} \frac{\partial}{\partial r} \left[r \varepsilon(T) \frac{\partial \psi}{\partial r} \right] + \frac{\partial}{\partial z} \left[\varepsilon(T) \frac{\partial \psi}{\partial z} \right] = - \frac{\sigma e (n_+ - n_-)}{\varepsilon_0} \quad (4-1)$$

The temperature-dependent dielectric constant of the electrolyte solution is assumed to be the same as that of water, and it can be formulated as (*Knox and McCormack*, 1994a)

$$\varepsilon(T) = 305.7 \exp \left(- \frac{T}{319} \right) \quad (4-2)$$

Introducing non-dimensional parameters

$$\bar{r} = \frac{r}{R} \quad \bar{z} = \frac{z}{R} \quad \bar{\psi} = \frac{\sigma e \psi}{k_b T} \quad \bar{\varepsilon} = \frac{\varepsilon(T)}{\varepsilon_{ref}} \quad \bar{n}_+ = \frac{n_+}{n_0} \quad \bar{n}_- = \frac{n_-}{n_0} \quad (4-3)$$

Eq. (4-1) can be further expressed in dimensionless form

$$\frac{1}{\bar{r}} \frac{\partial}{\partial \bar{r}} \left[\bar{r} \bar{\varepsilon} \frac{\partial \bar{\psi}}{\partial \bar{r}} \right] + \frac{\partial}{\partial \bar{z}} \left[\bar{\varepsilon} \frac{\partial \bar{\psi}}{\partial \bar{z}} \right] = - \frac{(\kappa R)^2}{2} (\bar{n}_+ - \bar{n}_-) \quad (4-4)$$

where ε_{ref} is dielectric constant of the solution at room temperature (i.e., $T_0 = 25^\circ \text{C}$), and it is chosen to be 78.5 in all the computation unless specified otherwise.

$\kappa = \left(\frac{2n_0 \sigma^2 e^2}{\varepsilon_{ref} \varepsilon_0 k_b T} \right)^{\frac{1}{2}}$ is the Debye-Hückel parameter, and its reciprocal represents the

EDL thickness. In the literature, κR is called the electrokinetic radius which characterizes the ratio of the geometric dimension to the EDL thickness, and hence denotes the relative contribution of the EDL effect.

4.2.2 Laplace equation

$$\frac{1}{r} \frac{\partial}{\partial r} \left[r \lambda(T) \frac{\partial \phi}{\partial r} \right] + \frac{\partial}{\partial z} \left[\lambda(T) \frac{\partial \phi}{\partial z} \right] = 0 \quad (4-5)$$

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In Eq. (4-5), the electrical conductivity of the general salt solution, $\lambda(T)$, is given as (Weast *et al*, 1986).

$$\lambda(T) = \lambda_+(T)\eta_+ + \lambda_-(T)\eta_- \quad (4-6a)$$

$$\lambda_+(T) = \lambda_{+0} + 0.025\lambda_{+0}(T - 298) \quad (4-6b)$$

$$\lambda_-(T) = \lambda_{-0} + 0.025\lambda_{-0}(T - 298) \quad (4-6c)$$

Here $\lambda_+(T)$ and $\lambda_-(T)$ are ionic conductivity of the cations and anions of the electrolyte at temperature T , λ_{+0} and λ_{-0} are ionic conductivity of the cations and anions of the electrolyte at the room temperature (i.e. 25 °C or 298 K), respectively, η_+ and η_- respectively denote the mole concentration of the cations and anions of the electrolyte.

Introducing non-dimensional parameters

$$\bar{r} = \frac{r}{R} \quad \bar{z} = \frac{z}{R} \quad \bar{\phi} = \frac{\phi}{\phi_{ref}} \quad \bar{\lambda} = \frac{\lambda(T)}{\lambda_0} \quad (4-7)$$

Eq. (4-5) can be further expressed in dimensionless form as

$$\frac{1}{r} \frac{\partial}{\partial r} \left[r \bar{\lambda} \frac{\partial \bar{\phi}}{\partial r} \right] + \frac{\partial}{\partial z} \left[\bar{\lambda} \frac{\partial \bar{\phi}}{\partial z} \right] = 0 \quad (4-8)$$

where ϕ_{ref} is the reference electric potential, generally refers to the difference of the applied electric potential between the inlet and outlet, that is, $\phi_{ref} = \phi_2 - \phi_1$, and $\lambda_0 = (\lambda_{+0} + \lambda_{-0})C$, is the electrical conductivity of the electrolyte solution at the room temperature, and here C is the mole concentration of the electrolyte solution.

4.2.3 Navier-Stokes equations

Continuity equation

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$$\frac{1}{r} \frac{\partial}{\partial r}(rv) + \frac{\partial u}{\partial z} = 0 \quad (4-9)$$

Momentum equations

$$\begin{aligned} \rho \left[v \frac{\partial u}{\partial r} + u \frac{\partial u}{\partial z} \right] = \\ - \frac{\partial p}{\partial z} + \frac{1}{r} \frac{\partial}{\partial r} \left[r \mu(T) \frac{\partial u}{\partial r} \right] + \frac{\partial}{\partial z} \left[\mu(T) \frac{\partial u}{\partial z} \right] + \rho_e E_z \end{aligned} \quad (4-10a)$$

$$\begin{aligned} \rho \left[v \frac{\partial v}{\partial r} + u \frac{\partial v}{\partial z} \right] = \\ - \frac{\partial p}{\partial r} + \frac{\partial}{\partial r} \left[\frac{\mu(T)}{r} \frac{\partial(rv)}{\partial r} \right] + \frac{\partial}{\partial z} \left[\mu(T) \frac{\partial v}{\partial z} \right] + \rho_e E_r \end{aligned} \quad (4-10b)$$

$$E_z = -\frac{\partial \phi}{\partial z} \quad E_r = -\frac{\partial \phi}{\partial r} \quad (4-10c)$$

where u and v are the velocity of the electroosmotic flow in axial direction and radial direction, respectively, and E_z and E_r are the applied electric field strength in axial direction and radial direction, respectively,

The above governing equations can be non-dimensionalized by introducing the following dimensionless parameters

$$\begin{aligned} \bar{r} = \frac{r}{R} \quad \bar{z} = \frac{z}{R} \quad \bar{\phi} = \frac{\phi}{\phi_{ref}} \quad \bar{u} = \frac{u}{U_{ref}} \quad \bar{v} = \frac{v}{U_{ref}} \quad \bar{E}_z = \frac{E_z}{E_0} \quad \bar{E}_r = \frac{E_r}{E_0} \\ \bar{P} = \frac{p}{\rho U_{ref}^2} \quad \bar{\mu} = \frac{\mu(T)}{\mu_{ref}} \quad \text{Re} = \frac{\rho R U_{ref}}{\mu_{ref}} \end{aligned} \quad (4-11)$$

where $U_{ref} = -\frac{\varepsilon_r \varepsilon_0 \zeta E_z}{\mu}$ is the Smoluchowski velocity (*Probstein, 1994*) and is

selected as the reference velocity in the calculation, and μ_{ref} is the reference dynamic viscosity. Re is the Reynolds number. E_0 is the reference applied electric field strength,

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generally refers to the average gradient of applied electric potential between the inlet and outlet; that is, the ratio of the difference of the applied electric potential to the length of the channel, $E_0 = \frac{\phi_2 - \phi_1}{L}$. Therefore, Eq. (4-9) and Eq. (4-10) in dimensionless form are expressed as

$$\frac{1}{r} \frac{\partial}{\partial r} (r \bar{v}) + \frac{\partial \bar{u}}{\partial z} = 0 \quad (4-12)$$

$$\begin{aligned} & \bar{u} \frac{\partial \bar{u}}{\partial z} + \bar{v} \frac{\partial \bar{u}}{\partial r} \\ &= -\frac{\partial \bar{p}}{\partial z} + \frac{1}{\text{Re}} \left\{ \frac{1}{r} \frac{\partial}{\partial r} \left[r \bar{\mu} \frac{\partial \bar{u}}{\partial r} \right] + \frac{\partial}{\partial z} \left[\bar{\mu} \frac{\partial \bar{u}}{\partial z} \right] \right\} + B_1 \bar{E}_z (\bar{n}_+ - \bar{n}_-) \end{aligned} \quad (4-13a)$$

$$\begin{aligned} & \bar{u} \frac{\partial \bar{u}}{\partial z} + \bar{v} \frac{\partial \bar{v}}{\partial r} \\ &= -\frac{\partial \bar{p}}{\partial r} + \frac{1}{\text{Re}} \left\{ \frac{\partial}{\partial r} \left[\frac{\bar{\mu}}{r} \frac{\partial (r \bar{v})}{\partial r} \right] + \frac{\partial}{\partial z} \left[\bar{\mu} \frac{\partial \bar{v}}{\partial z} \right] \right\} + B_1 \bar{E}_r (\bar{n}_+ - \bar{n}_-) \end{aligned} \quad (4-13b)$$

$$\bar{E}_z = -\frac{\phi_{ref}}{RE_0} \frac{\partial \bar{\phi}}{\partial z} \quad \bar{E}_r = -\frac{\phi_{ref}}{RE_0} \frac{\partial \bar{\phi}}{\partial r} \quad (4-13c)$$

$$B_1 = \frac{R \sigma e n_0 E_0}{\rho U_{ref}^2} \quad (4-13d)$$

where B_1 is dimensionless parameters, and it physically represents the ratio of the ionic electrostatic energy to kinetic energy.

4.2.4 Energy equation

$$\rho c_p \left(v \frac{\partial T}{\partial r} + u \frac{\partial T}{\partial z} \right) = \frac{1}{r} \frac{\partial}{\partial r} \left[r k_l(T) \frac{\partial T}{\partial r} \right] + \frac{\partial}{\partial z} \left[k_l(T) \frac{\partial T}{\partial z} \right] + \lambda(T) E^2 \quad (4-14a)$$

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$$E = \sqrt{E_z^2 + E_r^2} \quad (4-14b)$$

The energy equations can be non-dimensionalized by introducing the following dimensionless parameters

$$\begin{aligned} \bar{r} &= \frac{r}{R} & \bar{z} &= \frac{z}{R} & \bar{u} &= \frac{u}{U_{ref}} & \bar{v} &= \frac{\bar{v}}{U_{ref}} & \bar{\mu} &= \frac{\mu(T)}{\mu_{ref}} & \bar{k}_l &= \frac{k_l(T)}{k_{ref}} & \bar{\lambda} &= \frac{\lambda(T)}{\lambda_0} \\ \bar{E} &= \frac{E}{E_0} & \bar{T} &= \frac{T - T_{ref}}{T_0 - T_{ref}} & \text{Re} &= \frac{\rho R U_{ref}}{\mu_{ref}} & \text{Pr} &= \frac{\mu_{ref}}{k_{ref}/c_p} \\ Jo &= \frac{R^2 \lambda_0 E_0^2}{k_{ref} (T_0 - T_{ref})} \end{aligned} \quad (4-15)$$

where k_{ref} and T_{ref} are reference thermal conductivity and temperature, respectively.

Pr is the Prandtl number, which denotes the ratio of kinematic viscosity to thermal diffusivity. The parameter Jo referred to as Joule number in this work, reflects the importance of Joule heating and characterizes the ration of the Joule heating and the diffusion (conduction) heat. Therefore, energy equations in dimensionless form can be expressed as

$$\bar{u} \frac{\partial \bar{T}}{\partial \bar{z}} + \bar{v} \frac{\partial \bar{T}}{\partial \bar{r}} = \frac{1}{\text{Re Pr}} \left\{ \frac{1}{\bar{r}} \frac{\partial}{\partial \bar{r}} \left[\bar{r} \bar{k} \frac{\partial \bar{T}}{\partial \bar{r}} \right] + \frac{\partial}{\partial \bar{z}} \left[\bar{k} \frac{\partial \bar{T}}{\partial \bar{z}} \right] \right\} + \frac{Jo}{\text{Re Pr}} \bar{q} \quad (4-16a)$$

$$\bar{E} = \sqrt{\bar{E}_z^2 + \bar{E}_r^2} \quad (4-16b)$$

$$\bar{q} = \bar{\lambda} \cdot \bar{E}^2 \quad (4-16c)$$

4.2.5 Ionic concentration distribution

As mentioned earlier, in this section, the ionic concentration distributions are described using two models; namely the Nernst-Planck equation and the Boltzmann distribution.

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4.2.5.1 Nernst-Planck equation

Under a cylindrical coordinate system, the steady Nernst-Planck equation can be further expanded as

$$\begin{aligned}
 u \frac{\partial n_i}{\partial z} + v \frac{\partial n_i}{\partial r} = & \\
 \left[\frac{1}{r} \frac{\partial}{\partial r} \left(r D_i(T) \frac{\partial n_i}{\partial r} \right) + \frac{\partial}{\partial z} \left(D_i(T) \frac{\partial n_i}{\partial z} \right) \right] & \quad (4-17) \\
 + \left[\frac{1}{r} \frac{\partial}{\partial r} \left(r D_i(T) \frac{\sigma_i e n_i}{k_b T} \left(\frac{\partial \psi}{\partial r} - E_r \right) \right) + \frac{\partial}{\partial z} \left(D_i(T) \frac{\sigma_i e n_i}{k_b T} \left(\frac{\partial \psi}{\partial z} - E_z \right) \right) \right] &
 \end{aligned}$$

Generally, the temperature-dependent diffusion coefficient of the species can be described by the Stokes equation as

$$D_i(T) = \frac{k_b T}{6\pi\mu(T)r_s} \quad (4-18a)$$

where r_s is size of the species or particles.

According to *Weast et al.* (1986), the diffusion coefficient of the species, $D_i(T)$ can be simply expressed as

$$D_i(T) = D_{i0} + 0.025 D_{i0} (T - 298) \quad (4-18b)$$

where D_{i0} is the diffusion coefficient of the i th type ions at the room temperature (i.e. 25 °C or 298 K).

Introducing the following dimensionless parameters,

$$\begin{aligned}
 \bar{r} = \frac{r}{R} \quad \bar{z} = \frac{z}{R} \quad \bar{u} = \frac{u}{U_{ref}} \quad \bar{v} = \frac{v}{U_{ref}} \quad \bar{D}_i = \frac{D_i(T)}{D_{ref}} \quad \bar{\psi} = \frac{\sigma e \psi}{k_b T} \quad \bar{E}_z = \frac{E_z}{E_0} \\
 \bar{E}_r = \frac{E_r}{E_0} \quad Pe = \frac{R U_{ref}}{D_{ref}} \quad \bar{n}_i = \frac{n_i}{n_0} \quad (4-19)
 \end{aligned}$$

where, D_{ref} is the reference ionic diffusion coefficient and Pe is Peclet number.

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The cationic and anionic concentration distributions can be non-dimensionalised as

$$\begin{aligned} \frac{\bar{u}}{u} \frac{\partial \bar{n}_+}{\partial \bar{z}} + \frac{\bar{v}}{v} \frac{\partial \bar{n}_+}{\partial \bar{r}} = \frac{1}{Pe} \left\{ \left[\frac{1}{\bar{r}} \frac{\partial}{\partial \bar{r}} \left(\bar{r} \bar{D}_+ \frac{\partial \bar{n}_+}{\partial \bar{r}} \right) + \frac{\partial}{\partial \bar{z}} \left(\bar{D}_+ \frac{\partial \bar{n}_+}{\partial \bar{z}} \right) \right] + \right. \\ \left. \left[\frac{1}{\bar{r}} \frac{\partial}{\partial \bar{r}} \left(\bar{r} \bar{D}_+ \bar{n}_+ \left(\frac{\partial \bar{\psi}}{\partial \bar{r}} - B_2 \bar{E}_r \right) \right) + \frac{\partial}{\partial \bar{z}} \left(\bar{D}_+ \bar{n}_+ \left(\frac{\partial \bar{\psi}}{\partial \bar{z}} - B_2 \bar{E}_z \right) \right) \right] \right\} \end{aligned} \quad (4-20a)$$

$$\begin{aligned} \frac{\bar{u}}{u} \frac{\partial \bar{n}_-}{\partial \bar{z}} + \frac{\bar{v}}{v} \frac{\partial \bar{n}_-}{\partial \bar{r}} = \frac{1}{Pe} \left\{ \left[\frac{1}{\bar{r}} \frac{\partial}{\partial \bar{r}} \left(\bar{r} \bar{D}_- \frac{\partial \bar{n}_-}{\partial \bar{r}} \right) + \frac{\partial}{\partial \bar{z}} \left(\bar{D}_- \frac{\partial \bar{n}_-}{\partial \bar{z}} \right) \right] - \right. \\ \left. \left[\frac{1}{\bar{r}} \frac{\partial}{\partial \bar{r}} \left(\bar{r} \bar{D}_- \bar{n}_- \left(\frac{\partial \bar{\psi}}{\partial \bar{r}} - B_2 \bar{E}_r \right) \right) + \frac{\partial}{\partial \bar{z}} \left(\bar{D}_- \bar{n}_- \left(\frac{\partial \bar{\psi}}{\partial \bar{z}} - B_2 \bar{E}_z \right) \right) \right] \right\} \end{aligned} \quad (4-20b)$$

$$B_2 = \frac{R \sigma e E_0}{k_b T} \quad (4-20c)$$

where B_2 is a dimensionless parameter, and physically represents the ratio of the ionic electrostatic energy to the thermal energy.

4.2.5.2 Poisson – Boltzmann equation

Alternatively, for a symmetric electrolyte, the ionic concentration distributions are assumed to follow the Boltzmann distribution,

$$n_+ = n_0 \exp\left(-\frac{\sigma e \psi}{k_b T}\right) \quad n_- = n_0 \exp\left(\frac{\sigma e \psi}{k_b T}\right) \quad (4-21)$$

Using the dimensionless parameters defined in Eq. (4-19), Eq. (4-21) can also be non-dimensionalized as

$$\bar{n}_+ = \exp(-\bar{\psi}) \quad \bar{n}_- = \exp(\bar{\psi}) \quad (4-22)$$

Combining the Poisson equation with the Boltzmann distribution, we can get the non-dimensional Poisson – Boltzmann (P-B) equation as

$$\frac{1}{\bar{r}} \frac{\partial}{\partial \bar{r}} \left[\bar{r} \bar{\varepsilon} \frac{\partial \bar{\psi}}{\partial \bar{r}} \right] + \frac{\partial}{\partial \bar{z}} \left[\bar{\varepsilon} \frac{\partial \bar{\psi}}{\partial \bar{z}} \right] = (\kappa R)^2 \sinh(\bar{\psi}) \quad (4-23)$$

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Since the P-B equation is independent of the ionic concentration distributions, we can obtain the electrical potential distributions directly. It is much simpler than solving the coupling model on the basis of the Nernst-Planck equation.

4.2.6 Boundary conditions

The previous presented equations are subject to the following boundary conditions:

At the Inlet, $\bar{z} = 0$

$$\bar{T} = 1.0, \bar{\psi} = 0, \bar{\phi} = 1.0, \frac{\partial \bar{u}}{\partial \bar{z}} = 0, \frac{\partial \bar{v}}{\partial \bar{z}} = 0, \bar{n}_+ = 1.0, \bar{n}_- = 1.0 \quad (4-24a)$$

Since the channel length is assumed to be sufficiently long, the flow can achieve its fully developed state at the outlet, $\bar{z} = L/R$, and hence the outlet boundary conditions can be expressed as

$$\frac{\partial \bar{T}}{\partial \bar{z}} = 0, \frac{\partial \bar{\psi}}{\partial \bar{z}} = 0, \bar{\phi} = 0, \frac{\partial \bar{u}}{\partial \bar{z}} = 0, \frac{\partial \bar{v}}{\partial \bar{z}} = 0, \frac{\partial \bar{n}_+}{\partial \bar{z}} = 0, \frac{\partial \bar{n}_-}{\partial \bar{z}} = 0 \quad (4-24b)$$

Due to the symmetry, the boundary conditions at the cylinder centerline, $\bar{r} = 0$ are

$$\frac{\partial \bar{T}}{\partial \bar{r}} = 0, \frac{\partial \bar{\psi}}{\partial \bar{r}} = 0, \frac{\partial \bar{\phi}}{\partial \bar{r}} = 0, \frac{\partial \bar{u}}{\partial \bar{r}} = 0, \bar{v} = 0, \frac{\partial \bar{n}_+}{\partial \bar{r}} = 0, \frac{\partial \bar{n}_-}{\partial \bar{r}} = 0 \quad (4-24c)$$

At the capillary wall, $\bar{r} = 1$

$$\bar{\psi} = \bar{\zeta}, \bar{u} = 0, \frac{\partial \bar{\phi}}{\partial \bar{r}} = 0, \bar{v} = 0, \bar{n}_+ = \exp(-\bar{\zeta}), \bar{n}_- = \exp(\bar{\zeta}) \quad (4-24d)$$

where $\bar{\zeta}$ is the dimensionless zeta potential defined as $\bar{\zeta} = \sigma e \zeta / k_b T$.

In general, the temperature at the inner capillary wall is unknown. Since the heat generated by Joule heating and viscous dissipation in the electrolyte solution is mainly

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dissipated through the capillary wall to the surrounding environment, a conjugate heat transfer problem has to be solved to simultaneously account for heat transfer in both the liquid solution and the capillary wall. The governing dimensionless equation for heat conduction in the capillary wall is expressed as

$$\frac{1}{r} \frac{\partial}{\partial r} \left[\bar{r} \bar{k}_s \frac{\partial \bar{T}}{\partial r} \right] + \frac{\partial}{\partial z} \left[\bar{k}_s \frac{\partial \bar{T}}{\partial z} \right] = 0 \quad (4-25a)$$

where $\bar{k}_s$ is the dimensionless thermal conductivity of the glass capillary, and is also considered to be temperature-dependent.

The temperature boundary condition for the channel outside wall is given by

$$-\bar{k}_s \frac{\partial \bar{T}}{\partial r} \bigg|_{r=1+\Delta/R} = \frac{hR}{k_{ref}} (\bar{T} - 1) \quad (4-25b)$$

where h is the heat transfer coefficient outside the capillary.

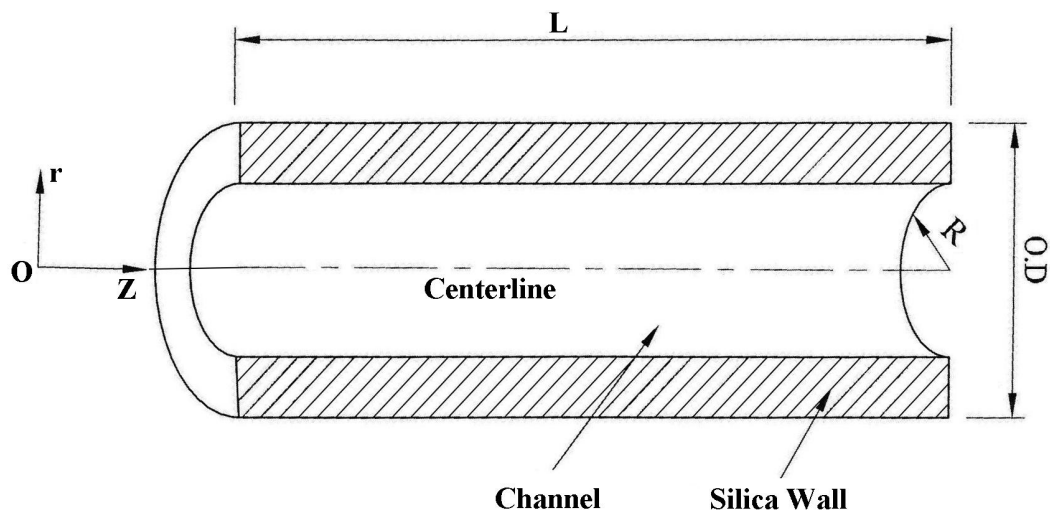


Fig. 4-1 Schematic diagram of the circular capillary.

4.3 Validation of the numerical method

To ensure the accuracy of the proposed numerical method, in the following section, the numerical method will be validated by comparing the numerical results with the analytical solutions which are available in the case of no Joule heating. Without Joule heating effect, no energy equation is present and all phenomenological coefficients are considered to be constant. Thus, the Poisson-Boltzmann equation and the fully developed Navier-Stokes equation are reduced to one-dimensional. Their analytical solutions for the EDL potential distribution and the electroosmotic flow field can be obtained. We therefore can numerically solve above simplified equations, and compare the numerical results with the analytical solutions to validate the numerical schemes.

4.3.1 Electrical potential

In the absence of Joule heating, the dimensionless Poisson-Boltzmann equation (4-23) can be simplified to one-dimensional, and expressed as

$$\frac{1}{\bar{r}} \frac{d}{d\bar{r}} \left[\bar{r} \frac{d\bar{\psi}}{d\bar{r}} \right] = (\kappa R)^2 \sinh(\bar{\psi}) \quad (4-26a)$$

Subject to the follow boundary conditions

$$\frac{d\bar{\psi}}{d\bar{r}} = 0 \quad \text{at } \bar{r} = 0, \quad \bar{\psi} = \bar{\zeta} \quad \text{at } \bar{r} = 1.0 \quad (4-26b)$$

where $\bar{\zeta}$ is the dimensionless zeta potential defined as $\bar{\zeta} = \sigma e \zeta / k_b T$.

According to *Kang et al.* (2002b), we can envisage the entire cylindrical region as comprising two hypothetical concentric regimes (Low potential and High potential), so that at their junctions (i.e., $\bar{r} = \bar{r}_j$), we have $\bar{\psi} = 1.0$. An analytical solution to equation (4-26) can be found as

$$\bar{\psi} = \frac{I_0(\kappa R \bar{r})}{I_0(\kappa R \bar{r}_j)} \quad (0 \leq \bar{r} \leq \bar{r}_j) \quad (4-27a)$$

$$\bar{\psi} = \ln \left\{ \frac{-C_n}{(\kappa R)^2 \bar{r}^2 \cos^2 \left[B + \frac{1}{2} \sqrt{-C_n} \ln(\bar{r}) \right]} \right\} \quad (\bar{r}_j \leq \bar{r} \leq 1.0) \quad (4-27b)$$

where I_0 and I_1 are the first kind, zero order and the first-kind, first-order modified Bessel function, respectively, and the parameters, B and C_n are given by

$$B = \cos^{-1} \sqrt{\frac{-C_n}{\exp(\bar{\zeta})(\kappa R)^2}}, \quad C_n = \left[2 + (\kappa R) \bar{r}_j \frac{I_1(\kappa R \bar{r}_j)}{I_0(\kappa R \bar{r}_j)} \right] + \exp(1) (\kappa R \bar{r}_j)^2 \quad (4-27c)$$

Fig. 4-2 shows the EDL potential profiles along the capillary radial direction obtained from the analytical solution and the numerical schemes. It is noted that the EDL potential exists only in the region in the vicinity of the channel wall, and decays very quickly from the zeta potential at the wall surface to zero outside the EDL. Further, examination of Fig. 4-2 indicates that the numerical solutions, calculated from both the Crank-Nicolson scheme and the power-law scheme, are almost indistinguishable from the analytical solutions, suggesting that the Power-law scheme and Crank-Nicolson scheme are both adequately accurate for solving the Poisson-Boltzmann equation.

4.3.2 Electroosmotic flow velocity

According to *Yang et al.* (2001a), for an isothermal electroosmotic flow (i.e., no Joule heating effect), the hydrodynamic entrance region is less than $0.1 R$. Such entrance effect is negligible because for practical Biochip applications, the ratio of the channel length to radius, L/R is very large. In other words, the electroosmotic flow can be considered as fully developed. Then the Navier-Stokes equation is also reduced to one-dimensional, and its dimensionless form can be expressed as

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$$\frac{1}{\text{Re}} \left[\frac{1}{\bar{r}} \frac{d}{d\bar{r}} \left(\bar{r} \frac{d\bar{u}}{d\bar{r}} \right) \right] - B_3 \sinh(\bar{\psi}) = 0 \quad (4-28a)$$

Subject to the following boundary conditions

$$\frac{d\bar{u}}{d\bar{r}} = 0 \quad \text{at } \bar{r} = 0 \quad \bar{u} = 0 \quad \text{at } \bar{r} = 1.0 \quad (4-28b)$$

where $B_3 = \frac{R \sigma e n_0 E_z}{\rho U_{ref}^2 / 2}$ is non-dimensional parameters. Similar to the dimensionless parameters B_1 , it physically represents the ratio of the ionic electrostatic energy to kinetic energy.

Combining with equation (4-26a), an exact solution of equation (4-28a) subject to the boundary conditions specified in equations (4-26b) and (4-28b) can be obtained

$$\bar{u} = \left(1 - \frac{\bar{\psi}}{\zeta} \right) \quad (4-29)$$

Fig. 4-3 shows the *EOF* velocity profiles along the capillary radial direction obtained from the analytical solution and the numerical schemes. Similar to the *EDL* potential profiles presented in Fig. 4-2, in Fig 4-3 three plots, representing the analytical solution and the numerical simulation results on the basis of the Crank-Nicolson scheme and the power-law scheme, collapse into one curve, indicating that the power-law scheme is comparable to the Crank-Nicolson scheme in this situation, and both give identical results to the analytical solution. This is anticipated because the Navier-Stokes equation that describes an isothermal electroosmotic flow in a microcapillary as shown in equation (4-28a) is also of pure diffusion type. Further, evaluation of Fig 4-3 shows that the EOF velocity profile exhibits a dramatic change, from zero (due to no-slip condition) to the reference velocity (i.e. Smoluchowski velocity) (as shown by equation (4-29)) within the EDL regime, and then keeps

unchanged throughout the rest of the capillary.

4.3.3 Temperature profile

In addition, to compare the Joule heating induced temperature distribution, we also did calculations based on the cases described in Table 4-1, which is published by *Grushka et al.* (1989). From the parameters listed in Table 4-1, we selected two radii in our calculation, $R = 50\mu m$ and $R = 125\mu m$. Other parameters are kept identical, including $\phi_2 - \phi_1 = 30kV$ for the channel with length of 1m ($E_0 = 30kV/m$), buffer concentration $C = 10^{-1}M$, and convection heat coefficient outside capillary $h = 10kW/(m^2 \cdot K)$. The numerical results are presented in Fig. 4-4 and Fig. 4-5, which show the radial temperature distributions in the capillary, solid wall, and coating layer in developed region for $R = 50\mu m$ and $R = 125\mu m$, respectively

Comparing the numerical results with the analytical solution provided in Table 4-1, it can be found that the numerical results obtained from both the Power-law scheme and the Crank-Nicolson scheme agree well with the analytical solution (see Table 4-2).

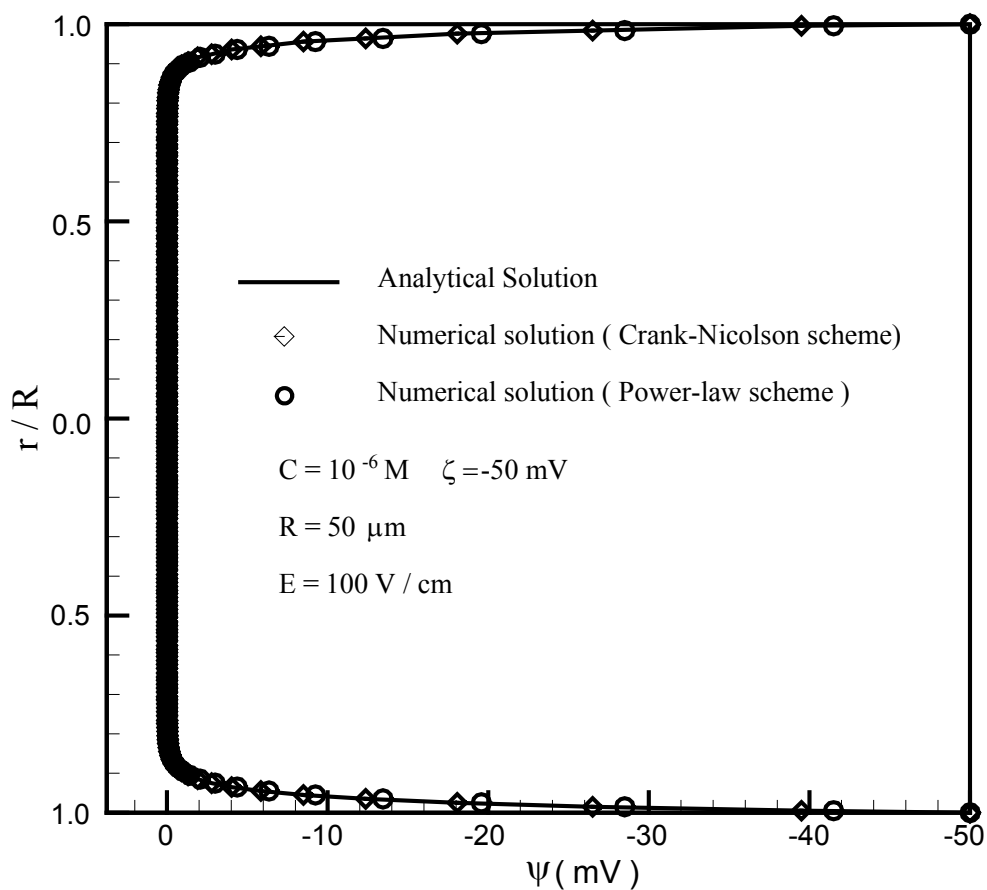


Fig. 4-2 Comparison of the radial distributions of the electrical double layer potential between the numerical simulation (based on both the Power-law scheme and the Crank-Nicolson scheme) and the analytical solution.

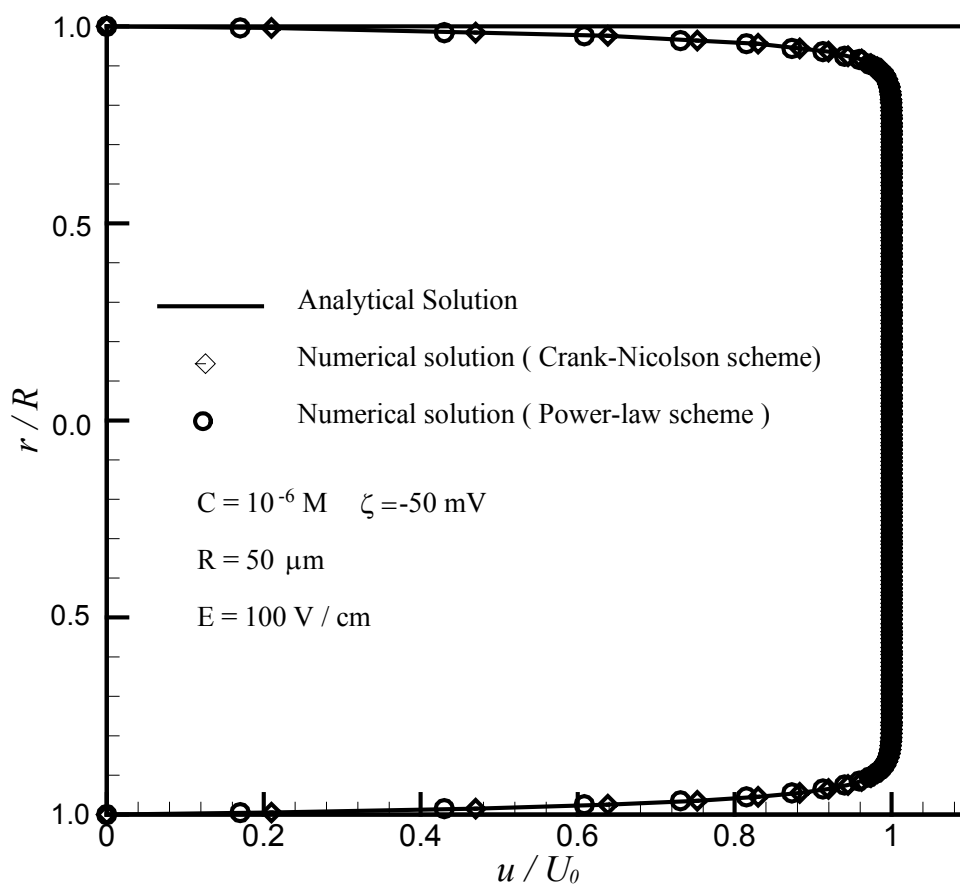


Fig. 4-3 Comparison of the radial distributions of the dimensionless fully-developed EOF velocity between the numerical simulation (based on both the Power-law scheme and the Crank-Nicolson scheme) and the analytical solution.

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Radius, μm	Wall temp, K	Temp diff, K
25	299.0	0.53
50	301.2	1.39
75	304.2	3.14
100	307.7	5.58
125	311.6	8.72
Parameters used: $V=30\text{ kV}$; $R_2 = 3.45 \times 10^{-4}\text{ m}$; $R_c = 3.75 \times 10^{-4}\text{ m}$; $T_a = 298\text{ K}$; $h = 10000\text{ W}/(\text{m}^2 \cdot \text{K})$; $k_1 = 0.605\text{ W}/(\text{m} \cdot \text{K})$; $k_2 = 1.5\text{ W}/(\text{m} \cdot \text{K})$; $B = 2400\text{ K}$; $D = 1 \times 10^{-9}\text{ m}^2/\text{s}$; $C_b = 100\text{ mol}/\text{m}^3$; $L = 1\text{ m}$		

Table 4-1 Capillary Internal Wall Temperature and Center-to-Wall Temperature Difference for Thermostated Capillaries published by *Grushka et al.* (1989)

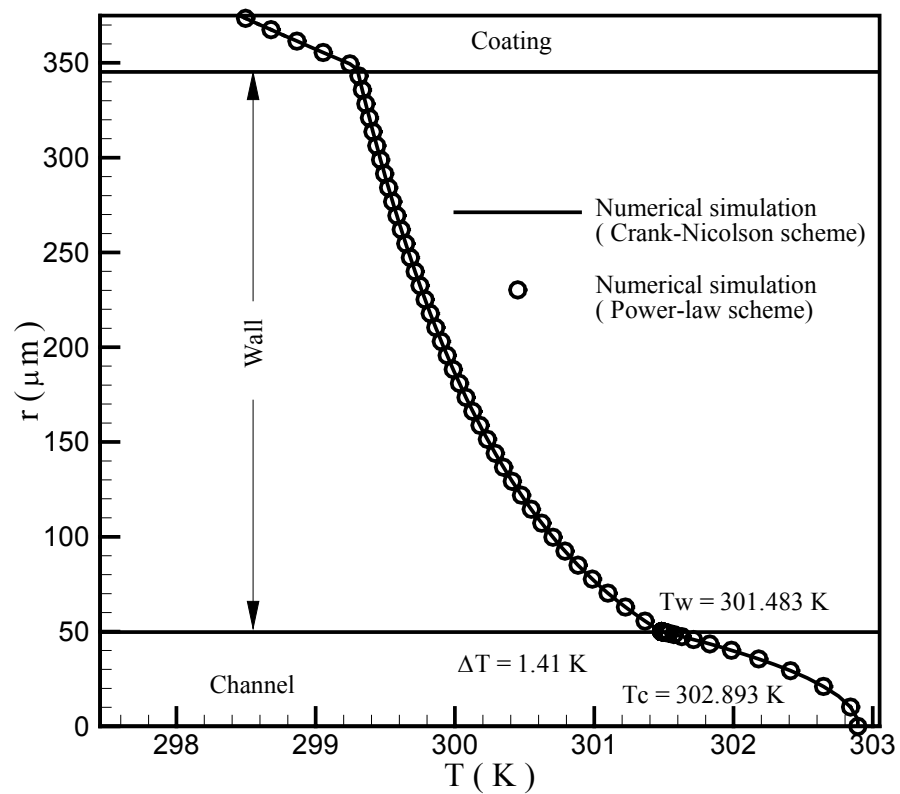


Fig. 4-4 Numerical simulation results of the radial temperature distributions in the capillary, solid wall, coating layer in developed region for $R = 50 \mu\text{m}$

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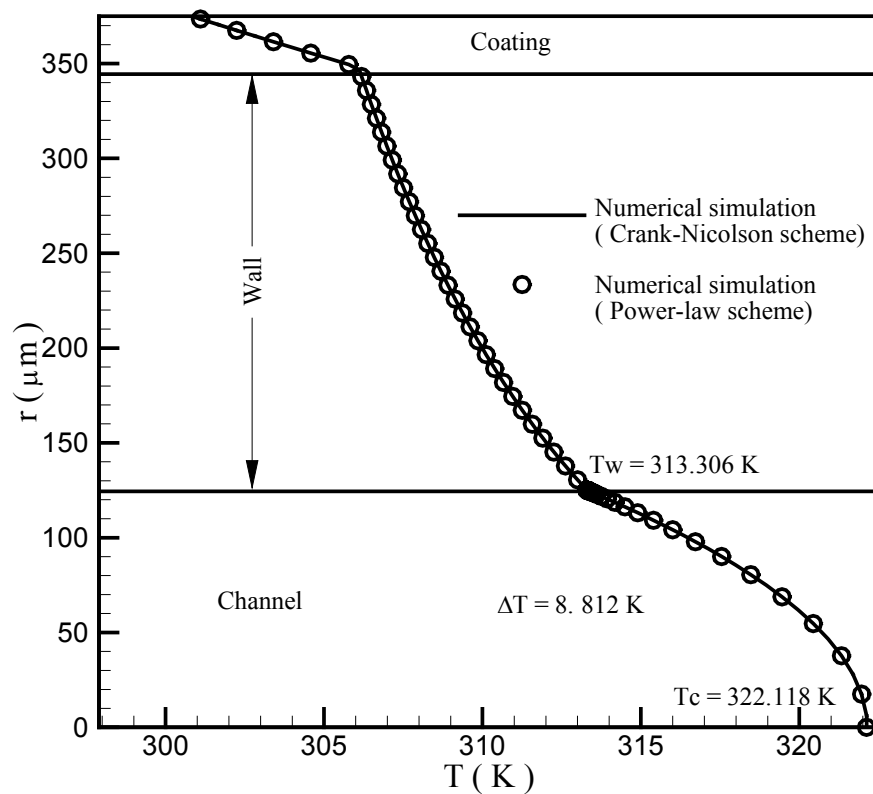


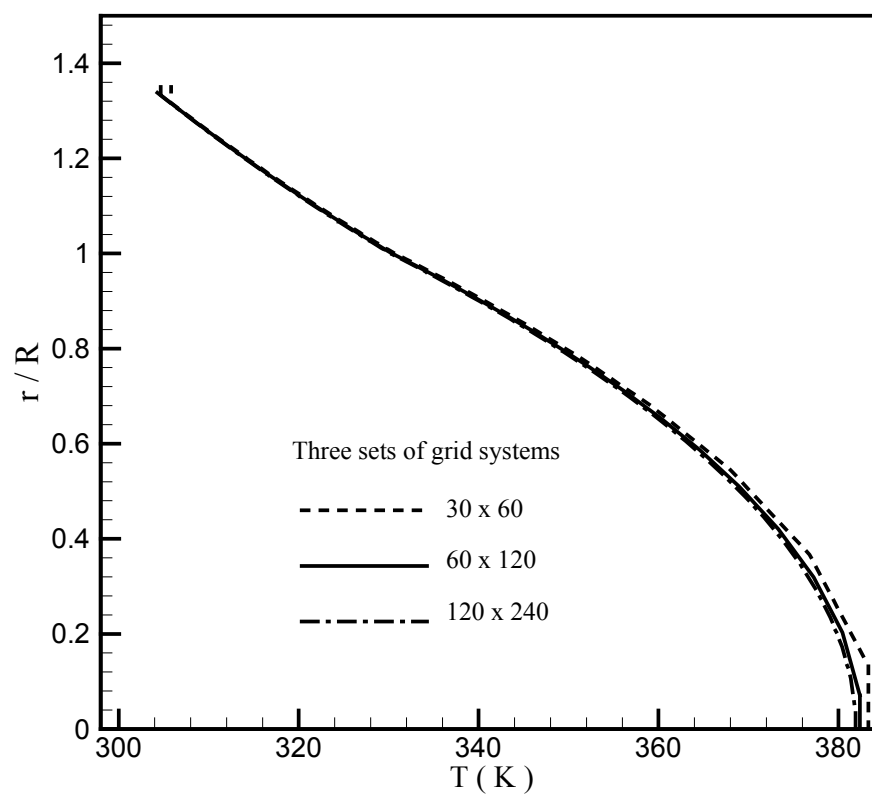
Fig. 4-5 Numerical simulation results of the radial temperature distributions in the capillary, solid wall, coating layer in developed region for $R = 125\mu m$

Radius, μm	Wall temp, K		Temp diff, K	
	Numerical	Analytical	Numerical	Analytical
50	301.483	301.2	1.41	1.39
125	313.306	311.6	8.812	8.72

Table 4-2 Comparison of the Joule heating induced temperature between the numerical results and analytical solutions

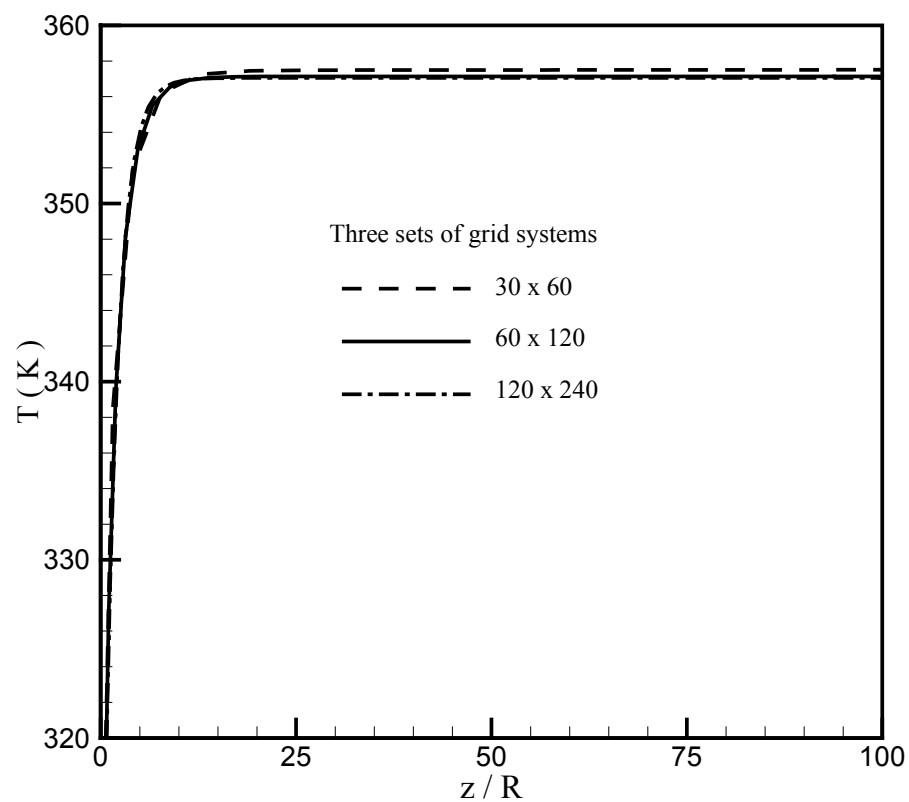
4.4 Grid size independence study

A grid size independence study is carried out using three sets of spatial grids. Fig. 4-6 shows (a) Radial temperature distributions in the liquid solution and channel solid wall in the fully developed region for different spatial grids and (b) Variation of solution mean temperature along the axial direction for different spatial grids. Fig. 4-7 shows the radial velocity distributions in the developed region for different spatial grids. First, the computation is carried out using a grid of 60 x 120 control volumes in the radial and axial directions, respectively. The number of control volumes in each direction are then increased to 120 x 240 control volumes and decreased to 30 x 60 control volumes. The calculation (Fig. 4-6 and Fig. 4-7) shows that when the spatial grids increase from 60 x 120 to 120 x 240, the numerical results have negligible change with the spatial grid. While when the spatial grids decrease from 60 x 120 to 30 x 60, the numerical results have noticeable changes with the spatial grids. This indicates that 60 x 120 control volumes in the radial and axial directions can produce grid independent solutions. As a result, the grids of 60 x 120 control volumes are chosen in all subsequence computations.



(a)

Fig. 4-6 Temperature distributions in the capillary for different spatial grids: (a) Radial temperature distributions in the capillary and its solid wall in developed region.



(b)

Fig. 4-6 Temperature distributions in the capillary for different spatial grids: (b)
Variation of solution mean temperature along the axial direction.

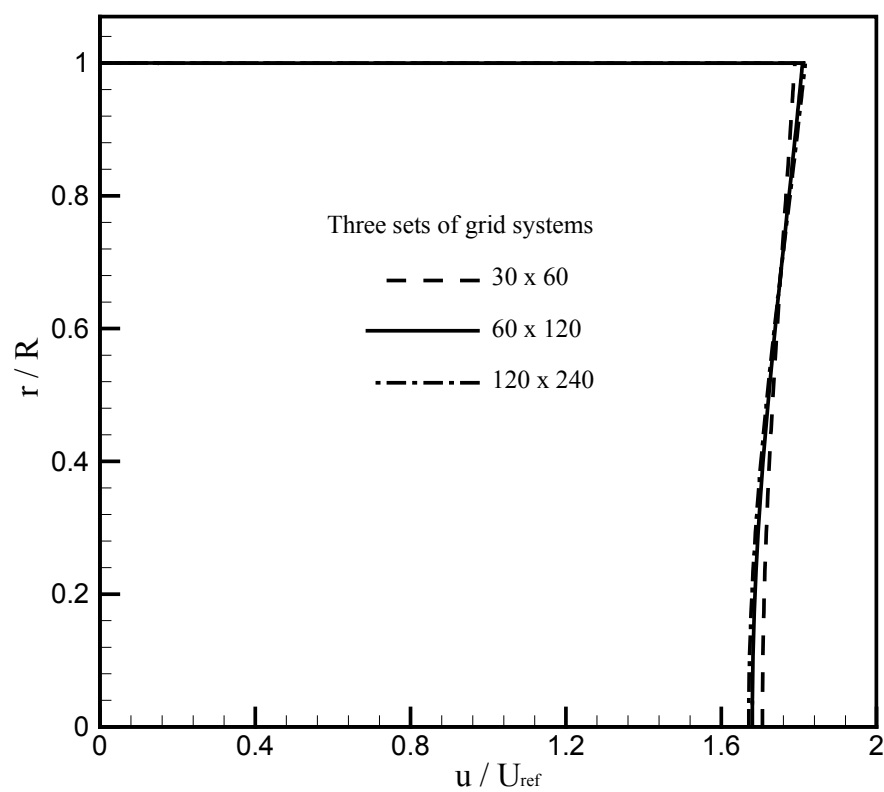


Fig. 4-7 The radial velocity distributions in the developed region for different spatial grids

4.5 Validation of the Boltzmann distribution (versus the Nernst-Planck equation)

It is well known that the EDL plays an important role in the EOF, and the parameter κ representing the reciprocal of the EDL thickness is one of the important parameters affected by the ionic concentration. According to the theory, the higher the buffer concentration, the larger the κ , or the thinner the EDL thickness. In addition, the microchannel size is also an important parameter affecting the EOF. Therefore, the product of κ and R is selected as the parameter to study the electrokinetic flow based on the Boltzman distribution and the Nernst-Planck equation.

In the calculations, κR is selected as 16, 500, and 5000, corresponding to a capillary of $10\mu m$ in diameter and electrolyte ionic concentrations of $10^{-6} M$, $10^{-3} M$ and $10^{-1} M$, respectively. The microcapillary is made of silica glass and has a length of $L = 50 mm$ and wall thickness of $\delta = 70 \mu m$ (Polymicro Technologies, USA). The working fluid is NaCl solution and its properties are: density $\rho = 998 kg/m^3$, electric conductivity at room temperature (298 K) $\lambda_{+0} = 50.08 \times 10^{-4} m^2 S/mol$ and $\lambda_{-0} = 76.31 \times 10^{-4} m^2 S/mol$, and the ionic diffuse coefficient at room temperature $D_{+0} = 1.334 \times 10^{-9} m^2/s$ and $D_{-0} = 2.032 \times 10^{-9} m^2/s$ (Weast et al, 1986).

4.5.1 Ionic concentration distribution

Figs. 4-8a-c show the steady-state radial distributions of dimensionless concentration (with respect to the bulk ionic concentration) for the co-ions and counter-ions at various axial locations with (a) $\kappa R = 16$, (b) $\kappa R = 500$ and (c) $\kappa R = 5000$, corresponding to the cases shown in Figs. 4-8a-c, respectively. From the EDL theoretical viewpoint, the diffuse layer of the EDL (or the extent of the EDL) is

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defined as such regime in which there are more counter-ions than co-ions, and hence the net charge density is not zero. Therefore, the dependence of the EDL regime and the development of the EDL in the presence of the flow on the electrokinetic diameter can be reflected from the radial distributions of the co-ions and counter-ions. It is noted from Fig. 4-8a that at the inlet region (i.e., small z/R values), the EDL (i.e., the regime where variation of ionic concentrations occurs) forms only in a very thin layer close to the capillary wall. As the flow develops (i.e., large z/R values), the variation of ion concentrations gradually extends to the center region of the capillary, indicating the EDL regime is getting larger with flow developing. Further, a comparison among Figs. 4-8a–c indicates that the EDL regime reduces as the electrokinetic diameter, κR increases.

Although Figs. 4-8a–c show that the ionic concentration spatial development patterns predicted by the Nernst-Planck equation and the Boltzmann distribution are similar, the difference of the two models and the effect of electrokinetic radius κR on the concentration distributions are clearly demonstrated. It can be seen that when the electrokinetic radius is small, e.g., $\kappa R = 16$, the radial distributions of ionic concentration obtained from the Nernst-Planck equation are different from those obtained from the Boltzmann equation within the entrance region (for example $z/R \leq 0.475$ when $\kappa R = 16$). Beyond such entrance region, no difference can be observed. As pointed out earlier, such difference occurring in the entrance region should be attributed to the flow development. When the electrokinetic radius is increased to $\kappa R = 500$, the influence of the *EOF* on the ionic concentration distributions reduces. As such, the entry region, in which the ionic concentration distributions obtained from the Nernst-Planck equation and the Boltzmann distribution are different, becomes smaller (see Fig. 4-8b). Further increment of the electrokinetic

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radius to $\kappa R = 5000$ makes the *EDL* become so thin that the effect of the EOF on the ionic concentration distributions inside the *EDL* regime is negligible. Therefore, as indicated in Fig. 4-8c, the difference of the co-ion and counter-ion distributions calculated by the Nernst-Planck equation and the Boltzmann distribution are virtually indistinguishable.

In addition, a comparison of co-ionic and counter-ionic concentration contours in the capillary obtained from the two different models is given in Fig. 4-9. It can be shown that in the hydrodynamically developed regime, the contour lines of the ionic concentration distributions are parallel to the channel wall, while in the hydrodynamically developing regime, the contour lines have steep slope. It hence indicates that the ionic concentration does not vary along the axial direction in the hydrodynamically developed regime, while varies in the hydrodynamically developing regime.

In our cases, the typical Reynolds number is of order 10^{-1} . For the ions in the electrolyte, the Schmidt number is smaller than 10^1 , and hence the Peclet number ($Sc \times Re$) is smaller than 1, suggesting that the contribution to the ionic concentration distributions due to hydrodynamic convection is smaller than that due to molecular diffusion. Since the major difference between the Nernst-Planck equation and the Boltzmann distribution lies in that the former takes care of the effect due to the hydrodynamic flow, both two models would give similar results of the ionic concentration distributions for the conditions considered in the case study.

4.5.2 Electrical potential field

The steady-state radial distributions of the electrical potential at different axial locations are respectively shown in Fig 4-10a-c for (a) $\kappa R = 16$, (b) $\kappa R = 500$ and (c)

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$\kappa R = 5000$. Other parameters used in the computation are $E = 500V/cm$, $\zeta = -50mV$, and $h = 10kW/m^2 K$. Physically the electric potential is induced due to the ion redistribution in the buffer solution. Theoretically, according to the Poisson equation, the electrical potential field is determined by the net charge density, which in turn depends on the distributions of co-ions and counter-ions in buffer solution. Hence, from Fig. 4-10a-c, we can find that the difference between the electrical potential distributions obtained from the Nernst-Planck equation and the Boltzmann distribution exhibits the same trend as that of the ionic distributions shown in Fig 4-8a-c.

4.5.3 Velocity field

Figs. 4-11a-c respectively show the steady-state radial distributions of dimensionless axial velocity (with respect to the reference velocity defined by using the Smoluchowski velocity ($U_{ref} = (\varepsilon_{ref} \varepsilon_0 / \mu_{ref}) E \zeta$) at various axial locations with (a) $\kappa R = 16$, (b) $\kappa R = 500$ and (c) $\kappa R = 5000$. Other parameters used in the computation are $E = 500V/cm$, $\zeta = -50mV$, and $h = 10W/m^2 K$. From Fig. 4-11a-c, we can find that the velocity distributions obtained by using the N-P equation and the Boltzmann distribution show no difference in the fully developed regime. While in the developing regime, the discrepancy of the velocity distribution using the two different models is observed. According to Eqs. (4-20a) and (4-20b), the *EOF* is induced by the interplay of the imposed electric field and the net charge density (defined in Eq. (2-10) and is related to the difference between counter-ions and co-ions within the *EDL*). Thus, the *EOF* velocity field is mainly determined by ionic concentration distributions. As a result, the effect of κR on the velocity distributions obtained from the two models exhibit the same tendency as that on the ionic concentration distributions shown in Figs.

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4-8a–c. For small κR (e.g., $\kappa R = 16$ and $\kappa R = 500$), the *EOF* velocity distributions shown in Figs. 4-11a and 4-11b predicted by the Nernst-Planck equation are different from those obtained from the Boltzmann distribution in the developing region, and such difference gradually disappears as κR increases. For very large κR , e.g., $\kappa R = 5000$, the velocity distributions calculated by the Nernst-Planck equations approach the results predicted by the Boltzmann distribution.

In addition, when the *EDL* thickness is comparable to the capillary radius, e.g., $\kappa R = 16$, one can observe (from Fig. 4-11a) how the *EOF* velocity develops spatially; it is in a similar fashion to that of the spatial development of the *EDL*. In the developing region, it is found that the velocity reaches the highest at a position near the capillary wall, and then gradually falls towards the capillary centerline. This scenario reveals the nature of the *EOF*; the driving force of the *EOF* only exists within the *EDL* regime, where the net charge density is not zero. The flow outside of the *EDL* regime in the capillary is attributed to hydrodynamic shear stress due to viscosity. Similar findings were also reported by Yang *et al.* (1998) without considering the Joule heating.

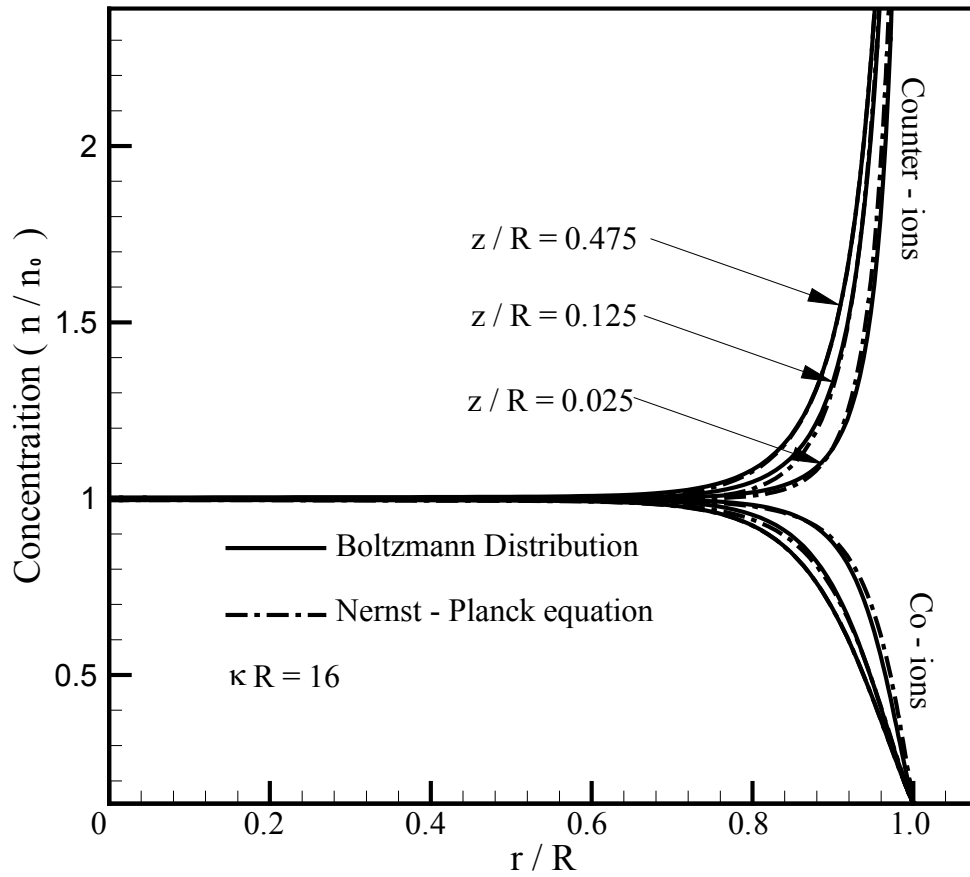
4.5.4 Temperature profile

Variation of the steady-state mean temperature profiles of the electrolyte along the axial direction for three different values of the electrokinetic radius, κR is shown in Fig. 4-12. It is noted that, for the lower values of κR , such as $\kappa R = 16$ and $\kappa R = 500$, the solution temperature virtually remains constant. This suggests in the cases of dilute electrolyte concentrations (e.g., less than $10^{-3} M$) or small capillary sizes (e.g., $10 \mu m$ in diameter), the Joule heating is negligible. While for higher values of κR , (e.g., 5000 or more), the Joule heating can be observed. However, the results of the mean temperature profile show no difference between the Nernst-Planck equation and the

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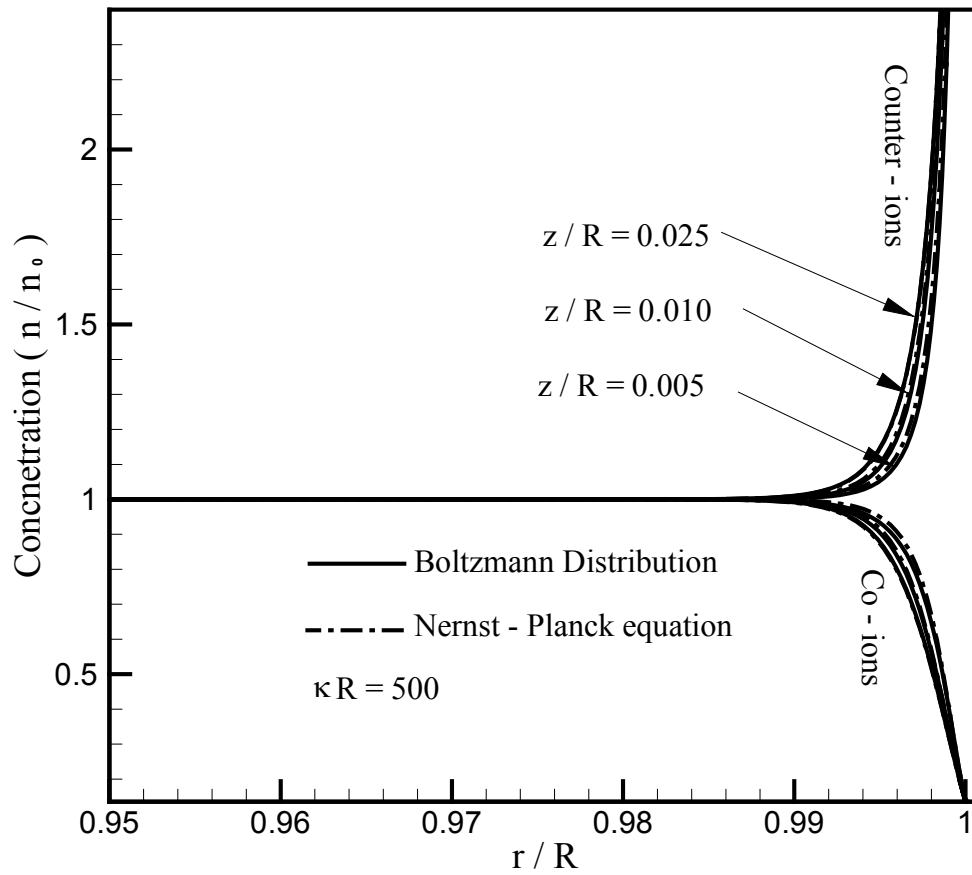
Boltzmann distribution. This is expected because in the case of $\kappa R = 5000$, both the Nernst-Planck equation and the Boltzmann distribution give the same results for both the ionic concentration distribution and the velocity field. Therefore, according to Eq. (4-16), the results of the temperature profiles obtained from the Nernst-Planck equation and the Boltzmann distribution should be identical.

From a practical viewpoint, the capillary electrophoresis is usually used to handle buffer solutions of at least $10^{-2} M$ in a capillary of $100\mu m$ in diameter, which corresponds to $\kappa R > 10000$. Therefore, based on the results presented in Figs. 4-8a-c, Figs. 4-11a-c, and Fig. 4-12, it can be concluded that as the Joule heating is concerned, the simple Boltzmann distribution is adequate in lieu of the general Nernst-Planck equation for estimating of the ionic concentration distribution, and hence, the *EOF* velocity field.



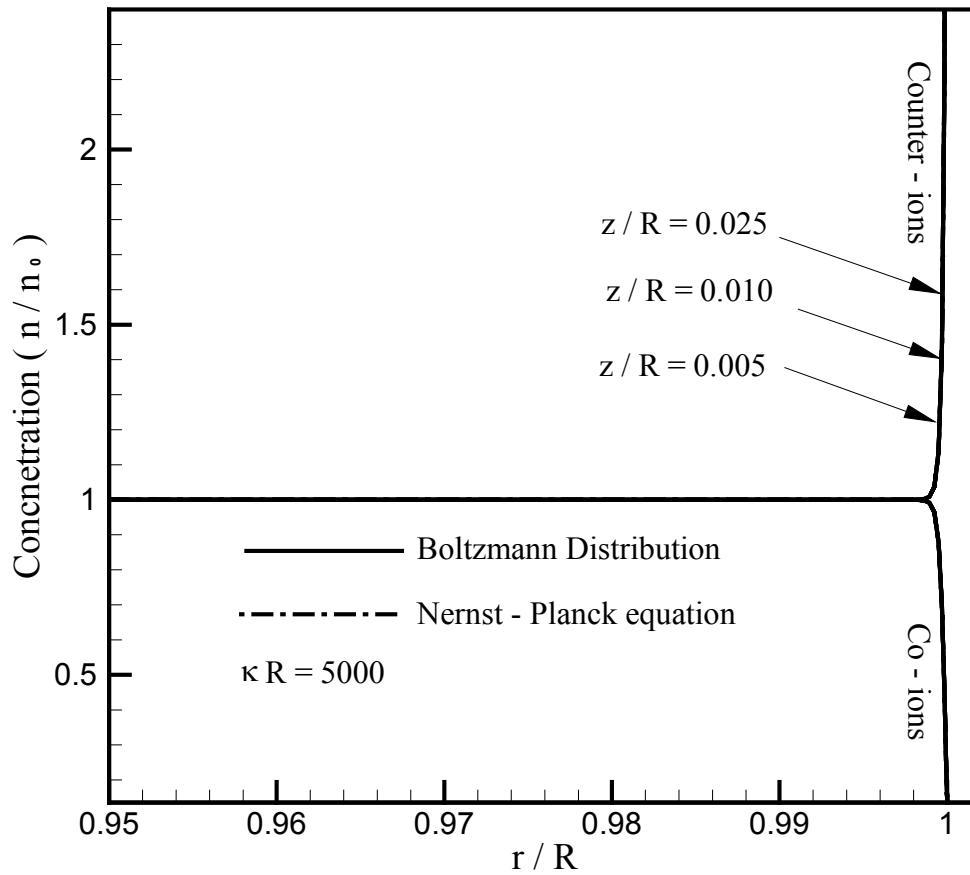
(a)

Fig. 4-8 Comparison of ionic concentration distributions between the P-B model and the N-P model at different axial positions when (a) $\kappa R = 16$; other parameters used in computations are $E = 500V/cm$, $\zeta = -50mV$, and $h = 10kW/m^2 K$.



(b)

Fig. 4-8 Comparison of ionic concentration distributions between the P-B model and the N-P model at different axial positions when (b) $\kappa R = 500$; other parameters used in computations are $E = 500V/cm$, $\zeta = -50mV$, and $h = 10kW/m^2 K$.



(c)

Fig. 4-8 Comparison of ionic concentration distributions between the P-B model and the N-P model at different axial positions when (c) $\kappa R = 5000$; other parameters used in computations are $E = 500V/cm$, $\zeta = -50mV$, and $h = 10kW/m^2 K$.

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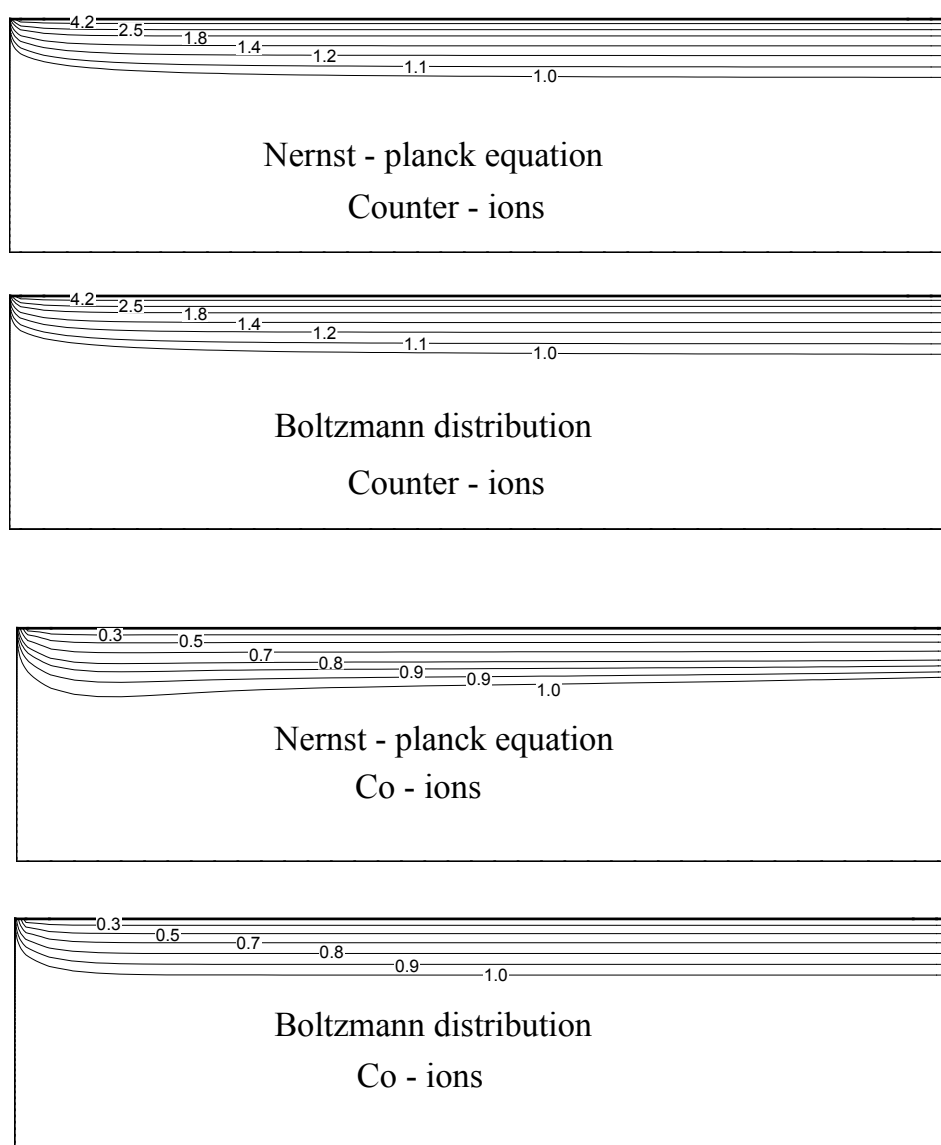
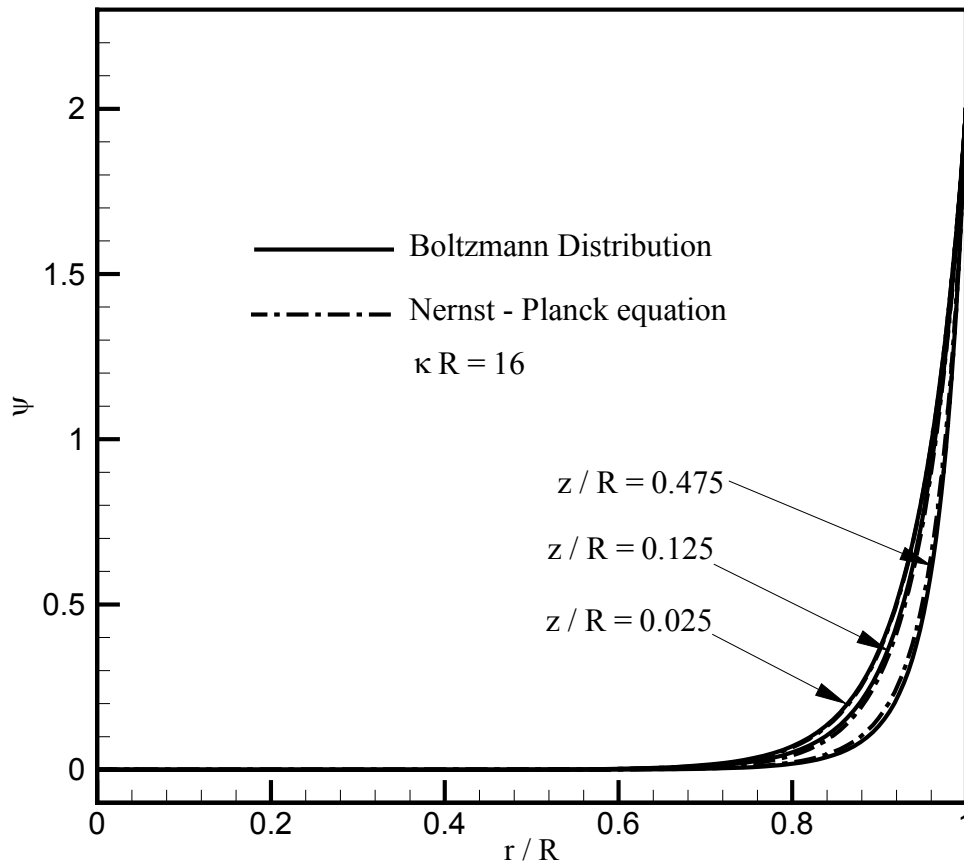
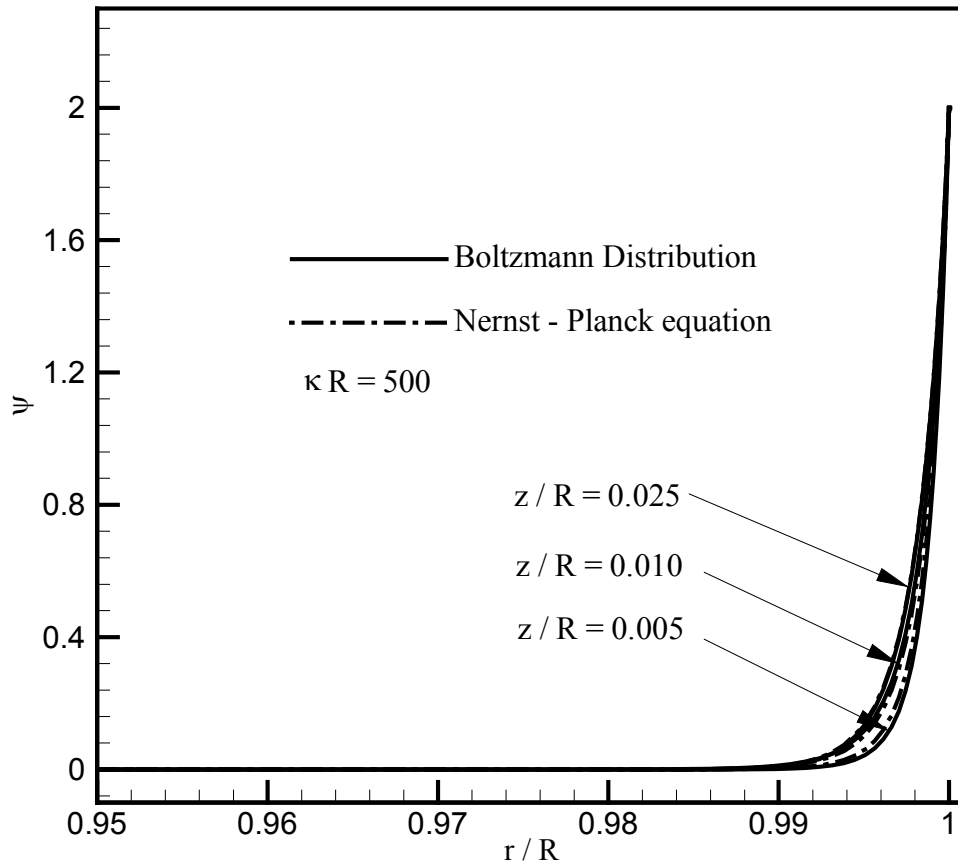


Fig. 4-9 Ionic concentration contour in the microcapillary at steady state when $\kappa R = 16$; other parameters used in computations are $E = 500V/cm$, $\zeta = -50mV$, and $h = 10kW/m^2 K$.



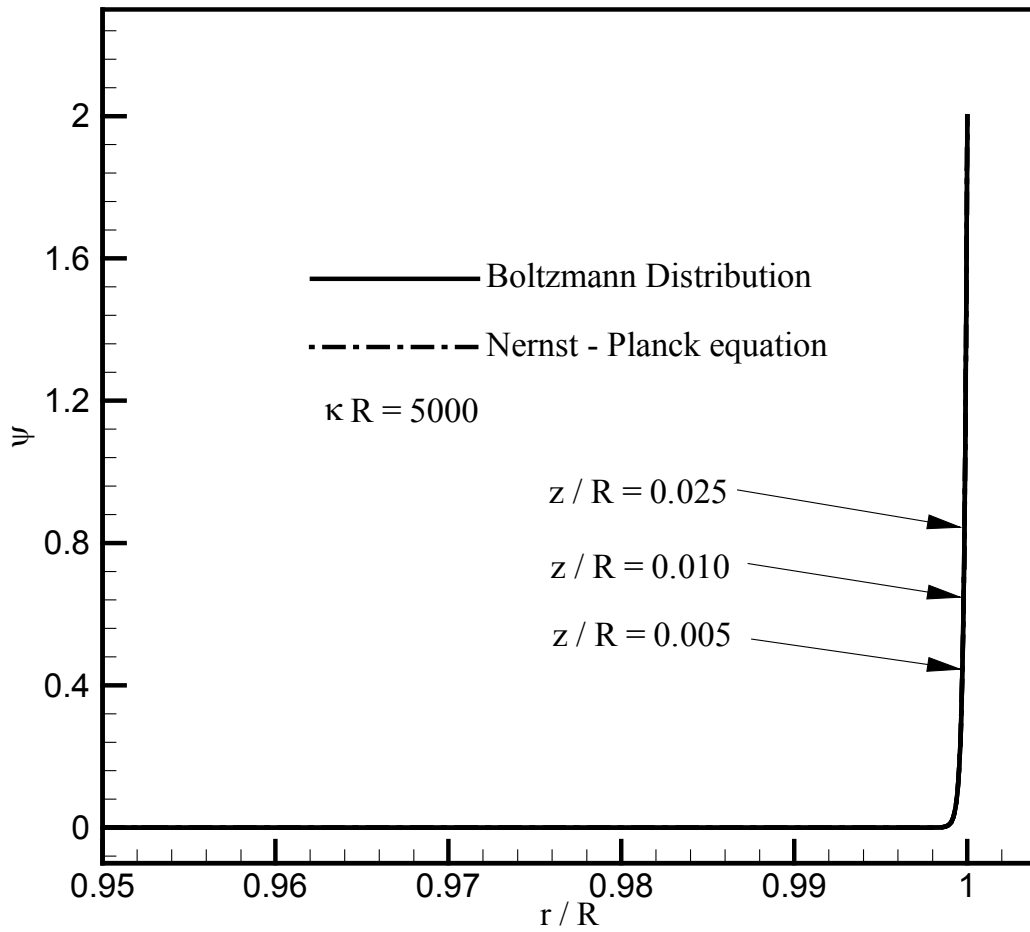
(a)

Fig. 4-10 Comparison of electrical potential distributions between the P-B model and the N-P model at different axial positions when (a) $\kappa R = 16$; other parameters used in computations are $E = 500V/cm$, $\zeta = -50mV$, and $h = 10kW/m^2 K$.



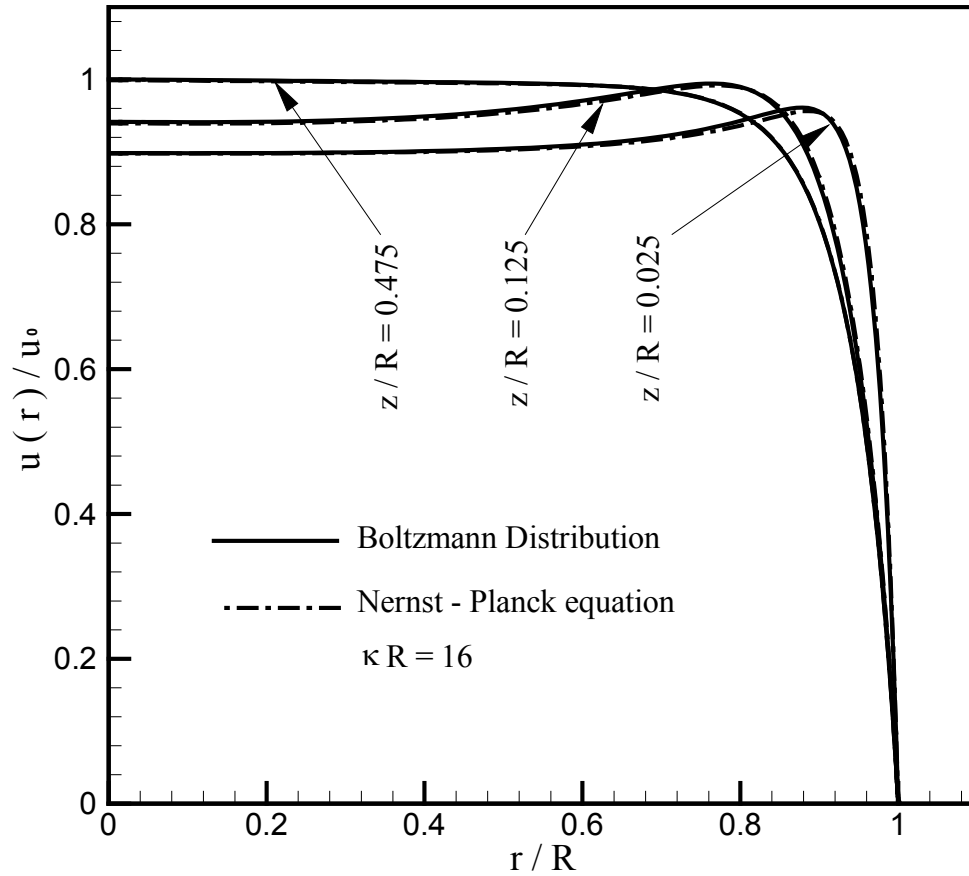
(b)

Fig. 4-10 Comparison of electrical potential distributions between the P-B model and the N-P model at different axial positions when (b) $\kappa R = 500$; other parameters used in computations are $E = 500V/cm$, $\zeta = -50mV$, and $h = 10kW/m^2 K$.



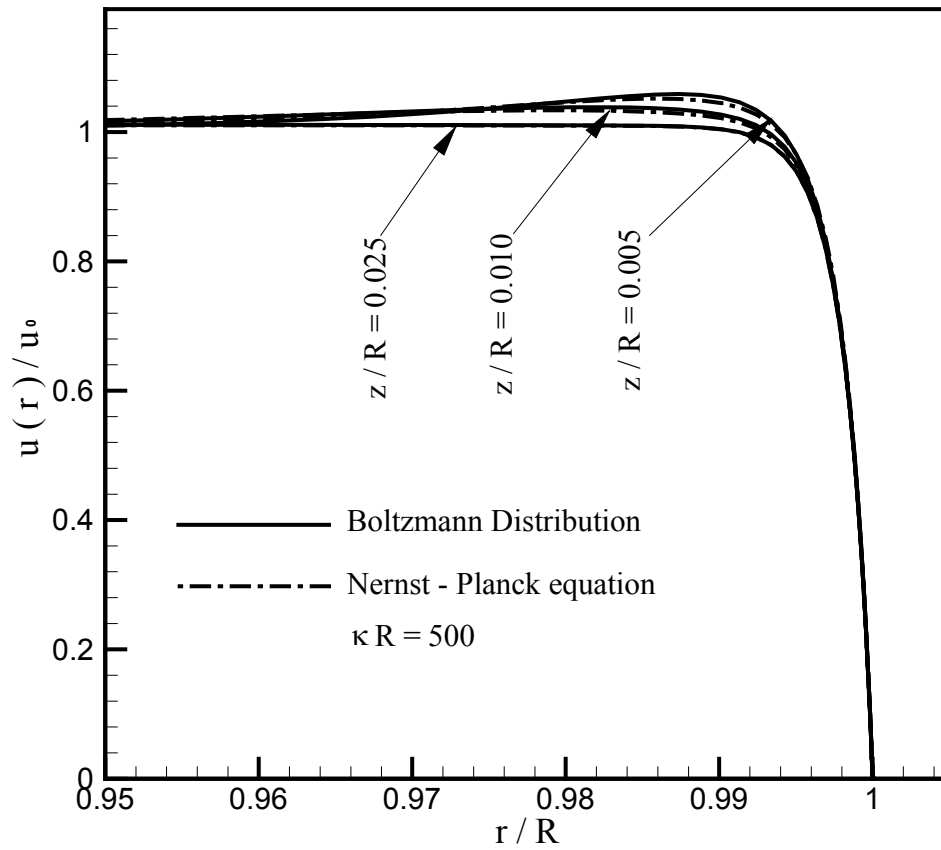
(c)

Fig. 4-10 Comparison of electrical potential distributions between the P-B model and the N-P model at different axial positions when (c) $\kappa R = 5000$; other parameters used in computations are $E = 500V/cm$, $\zeta = -50mV$, and $h = 10kW/m^2 K$.



(a)

Fig. 4-11 Comparison of the EOF velocity distributions between the P-B model and the N-P model at different axial positions when (a) $\kappa R = 16$; other parameters used in computations are $E = 500V/cm$, $\zeta = -50mV$, and $h = 10kW/m^2 K$.



(b)

Fig. 4-11 Comparison of the EOF velocity distributions between the P-B model and the N-P model at different axial positions when (b) $\kappa R = 500$; other parameters used in computations are $E = 500V/cm$, $\zeta = -50mV$, and $h = 10kW/m^2 K$.

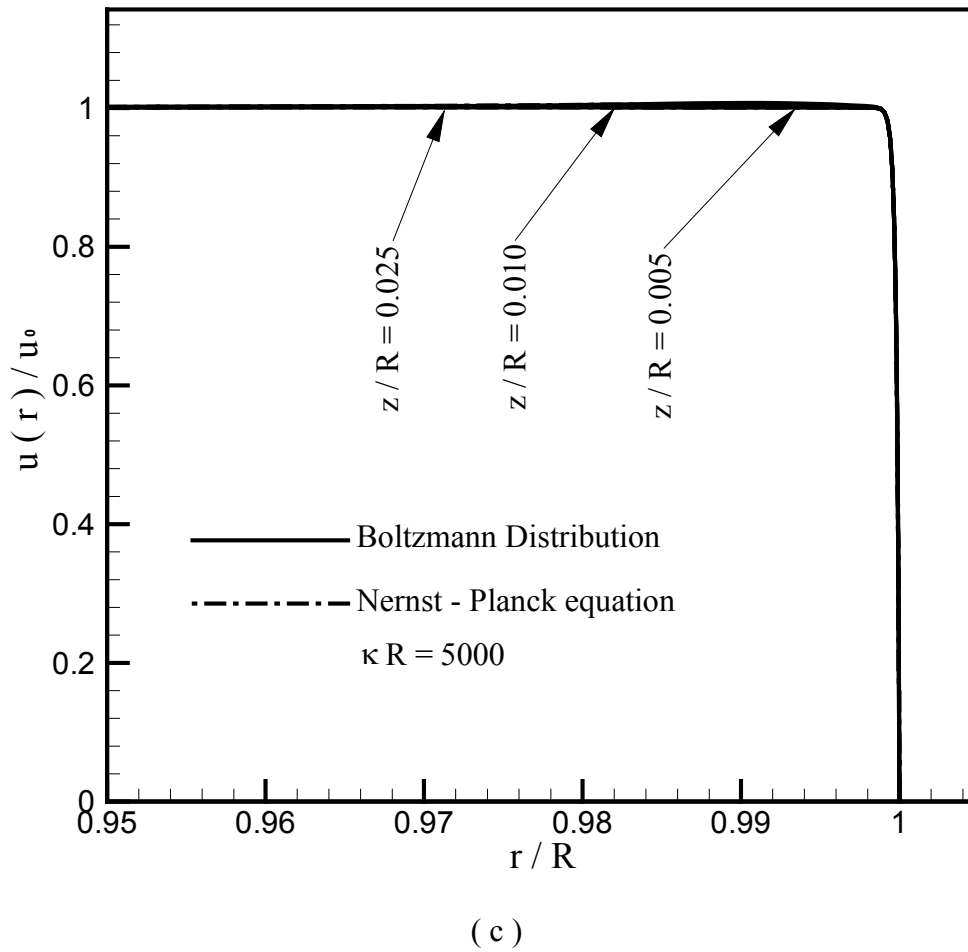


Fig. 4-11 Comparison of the EOF velocity distributions between the P-B model and the N-P model at different axial positions when (c) $\kappa R = 5000$; other parameters used in computations are $E = 500V/cm$, $\zeta = -50mV$, and $h = 10kW/m^2 K$.

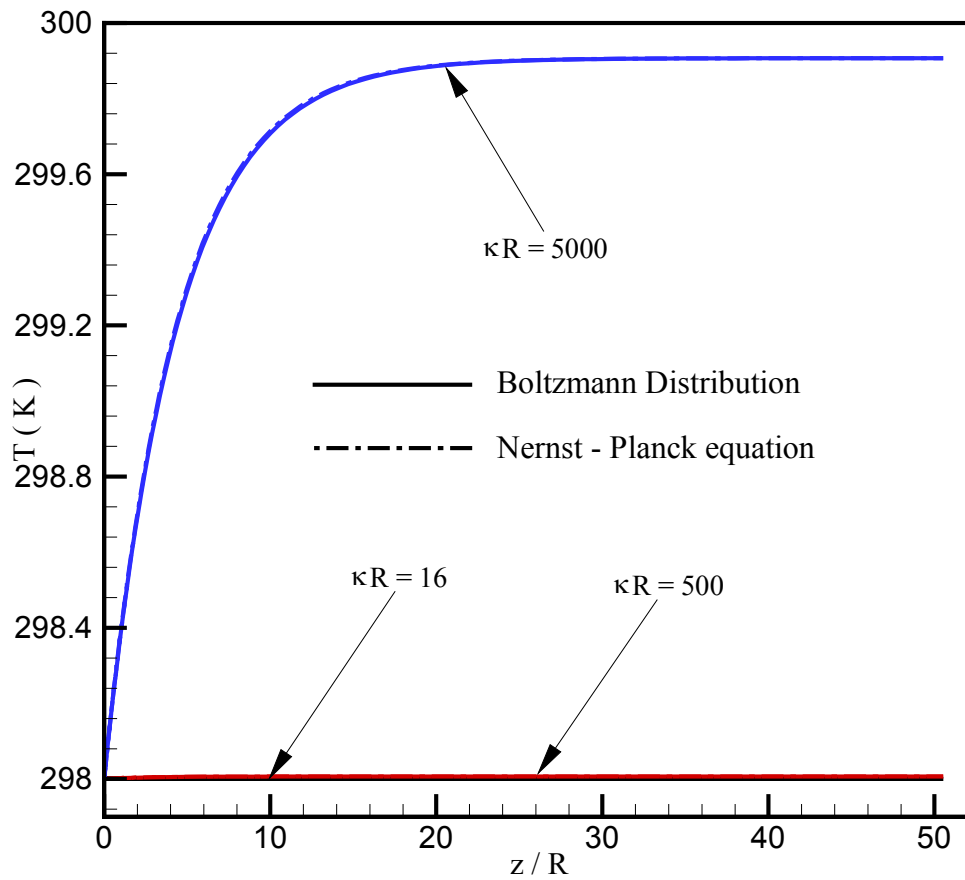


Fig. 4-12 The solution mean temperature profiles obtained from the N-P model and P-B model along the axial direction with different EDL thickness parameters, other parameters used in computations are $E = 500V/cm$, $\zeta = -50mV$, and $h = 10kW/m^2 K$.

4.6 Summary

In this chapter, a systematic study is carried out to evaluate the ionic concentration distributions in both the developing and the fully developed *EOF* regions on the basis of the Nernst-Planck equation and the Boltzmann distribution. According to the above results and discussion, it can be concluded that for low values of κR (e.g. $\kappa R = 16$), where the *EDL* plays an important role, in the *EOF* developing region the ionic concentration distribution predicted by the Nernst-Planck equation deviates from the Boltzmann distribution. As the *EOF* develops, the deviation becomes smaller, and finally in the *EOF* fully developed region, the Nernst-Planck equation gives the ionic concentration distribution the same as the Boltzmann distribution. For large values of κR (e.g. $\kappa R = 5000$), where the *EDL* regime is thin compared to the capillary radius, the Nernst-Planck equation and the Boltzmann distribution predict identical ionic concentration distributions in both developing and developed regions of the *EOF*. These findings suggest that when Joule heating is included, the κR usually is large, and simple Boltzmann distribution can be assumed. Hence, in the following chapters, the Joule heating and its effects will be evaluated on the basis of the Boltzmann distribution.

CHAPTER 5

JOULE HEATING AND ITS EFFECTS IN CAPILLARY ELECTROPHORETIC SYSTEMS

5.1 Introduction

As pointed out in chapter 1, the electrokinetic phenomena such as the electroosmotic flow and capillary electrophoresis are driven by an externally applied electric field. Therefore the induced Joule heating of the conductive electrolyte solution is inevitable. This is a major disadvantage to the application of electroosmotic flow and capillary electrophoresis, especially for large capillary size or high electrolyte concentration. Previous studies (*Knox and McCormack*, 1994a, 1994b) have amply demonstrated that the effects of Joule heating can result in low column separation efficiency, reduction of analysis resolution, and even loss of injected samples. In addition, temperature rise can lead to the decomposition of thermally labile samples and the formation of gas bubbles. Therefore it is important to control the temperature within the microfluidics systems.

Hence, the objective of this chapter is to provide an in-depth analysis of the Joule heating and its effects on the electroosmotic flow and capillary electrophoresis based on the mathematical models derived in earlier chapters, as such to increase our understanding of the thermal aspects of electroosmotic flow and electrophoresis. In this chapter, the problem of Joule heating in a capillary electrophoresis system is first formulated, and the theoretical models are presented. Then, the mathematical models are numerically solved using a finite-volume based CFD technique. Subsequently, the transient and steady state Joule heating and its effects on the electroosmotic flow in a capillary electrophoresis system are discussed. Computations for electrical potential,

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temperature, and velocity in a microcapillary are performed under the effects of the radius of capillary, concentration of electrolyte solution, strength of applied electrical field, and heat transfer coefficient outside capillary wall.

Realizing that electroosmotic flows are usually used for injection and separation of biological or chemical samples such as DNA sequencing in genetic engineering, the effect of Joule heating on the transport of sample species in capillary electrophoresis systems is also evaluated in this study.

5.2 Problem formulation

As mentioned in chapter 4, for the case of Joule heating, the κR usually is large, and the simple Boltzmann distribution can be safely assumed. The mathematical model development based on the Boltzmann distribution in this chapter is similar to that in the chapter 4. However, since the temperature development during electrokinetic mass transport can affect a myriad of phenomena such as dispersion, flow profiles, and partitioning of analytes between the mobile and stationary phase, hence the transient Joule heating and its effect on the electroosmotic flow in a capillary electrophoresis system will be studied in this chapter. the models developed in this chapter include the Poisson-Boltzmann (P-B) equation, the Laplace equation, the modified transient Navier-Stokes (N-S) equations and the transient energy equation.

Consider the electrokinetic flow in the capillary with inner radius of R and length of L in a commercially available capillary electrophoresis system as shown in Fig. 5-1. As mentioned earlier, due to the Joule heating induced temperature development imposing effects electrokinetic mass transport, the transient Joule heating and its effects will be studied. Hence the transient mathematical models will

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be presented in this section. Realizing that the time scale for the EDL is small due to the thin EDL layer, and hence the equations for EDL potential and applied electric potential can be considered to be at steady state. Therefore, using the same cylindrical coordinate system as presented in chapter 4, the dimensionless forms of the governing equations for a viscous Newtonian fluid of uniform and homogeneous composition can be given in the following sections.

5.2.1 Poisson-Boltzmann equation

$$\frac{1}{\bar{r}} \frac{\partial}{\partial \bar{r}} \left[\bar{r} \bar{\varepsilon} \frac{\partial \bar{\psi}}{\partial \bar{r}} \right] + \frac{\partial}{\partial \bar{z}} \left[\bar{\varepsilon} \frac{\partial \bar{\psi}}{\partial \bar{z}} \right] = (\kappa R)^2 \sinh(\bar{\psi}) \quad (5-1)$$

5.2.2 Laplace equation

$$\frac{1}{\bar{r}} \frac{\partial}{\partial \bar{r}} \left[\bar{r} \bar{\lambda} \frac{\partial \bar{\phi}}{\partial \bar{r}} \right] + \frac{\partial}{\partial \bar{z}} \left[\bar{\lambda} \frac{\partial \bar{\phi}}{\partial \bar{z}} \right] = 0 \quad (5-2)$$

5.2.3 Transient movement equations

$$\frac{1}{\bar{r}} \frac{\partial}{\partial \bar{r}} (\bar{r} \bar{v}) + \frac{\partial \bar{u}}{\partial \bar{z}} = 0 \quad (5-3)$$

$$\begin{aligned} & \frac{\partial \bar{u}}{\partial \bar{t}} + \bar{v} \frac{\partial \bar{u}}{\partial \bar{r}} + \bar{u} \frac{\partial \bar{u}}{\partial \bar{z}} \\ &= -\frac{\partial \bar{p}}{\partial \bar{z}} + \frac{1}{\text{Re}} \left\{ \frac{1}{\bar{r}} \frac{\partial}{\partial \bar{r}} \left[\bar{r} \bar{\mu} \frac{\partial \bar{u}}{\partial \bar{r}} \right] + \frac{\partial}{\partial \bar{z}} \left[\bar{\mu} \frac{\partial \bar{u}}{\partial \bar{z}} \right] \right\} - B_3 \bar{E}_z \sinh(\bar{\psi}) \end{aligned} \quad (5-4a)$$

$$\begin{aligned} & \frac{\partial \bar{v}}{\partial \bar{t}} + \bar{v} \frac{\partial \bar{v}}{\partial \bar{r}} + \bar{u} \frac{\partial \bar{v}}{\partial \bar{z}} \\ &= -\frac{\partial \bar{p}}{\partial \bar{r}} + \frac{1}{\text{Re}} \left\{ \frac{\partial}{\partial \bar{r}} \left[\frac{\bar{\mu}}{\bar{r}} \frac{\partial (\bar{r} \bar{v})}{\partial \bar{r}} \right] + \frac{\partial}{\partial \bar{z}} \left[\bar{\mu} \frac{\partial \bar{v}}{\partial \bar{z}} \right] \right\} - B_3 \bar{E}_r \sinh(\bar{\psi}) \end{aligned} \quad (5-4b)$$

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$$\bar{E}_z = -\frac{\phi_{ref}}{RE_0} \frac{\partial \bar{\phi}}{\partial \bar{z}} \quad \bar{E}_r = -\frac{\phi_{ref}}{RE_0} \frac{\partial \bar{\phi}}{\partial \bar{r}} \quad B_3 = \frac{R\sigma n_0 E_0}{\rho U_{ref}^2 / 2} \quad (5-4c)$$

5.2.4 Transient energy equation

$$\frac{\partial \bar{T}}{\partial \bar{t}} + \bar{v} \frac{\partial \bar{T}}{\partial \bar{r}} + \bar{u} \frac{\partial \bar{T}}{\partial \bar{z}} = \frac{1}{\text{Re Pr}} \left\{ \frac{1}{\bar{r}} \frac{\partial}{\partial \bar{r}} \left[\bar{r} \bar{k}_l \frac{\partial \bar{T}}{\partial \bar{r}} \right] + \frac{\partial}{\partial \bar{z}} \left[\bar{k}_l \frac{\partial \bar{T}}{\partial \bar{z}} \right] \right\} + \frac{Jo}{\text{Re Pr}} \bar{q} \quad (5-5a)$$

$$\bar{E} = \sqrt{\bar{E}_z^2 + \bar{E}_r^2} \quad \bar{q} = \bar{\lambda} \cdot \bar{E}^2 \quad (5-5b)$$

5.2.5 Initial and boundary conditions

The above equations are subject to the following initial and boundary conditions:

The initial conditions ($\bar{t} = 0$),

$$\bar{u} = 0 \quad \bar{v} = 0 \quad \bar{T} = 1.0 \quad (5-6a)$$

The boundary conditions,

At the Inlet ($\bar{z} = 0$),

$$\bar{T} = 1.0 \quad \bar{\psi} = 0 \quad \frac{\partial \bar{u}}{\partial \bar{z}} = 0 \quad \frac{\partial \bar{v}}{\partial \bar{z}} = 0 \quad \bar{\phi} = 1.0 \quad (5-6b)$$

At the outlet ($\bar{z} = L/R$),

$$\frac{\partial^2 \bar{T}}{\partial \bar{z}^2} = 0 \quad \frac{\partial \bar{\psi}}{\partial \bar{z}} = 0 \quad \frac{\partial \bar{u}}{\partial \bar{z}} = 0 \quad \frac{\partial \bar{v}}{\partial \bar{z}} = 0 \quad \bar{\phi} = 0.0 \quad (5-6c)$$

At the cylinder centerline ($\bar{r} = 0$),

$$\frac{\partial \bar{T}}{\partial \bar{r}} = 0 \quad \frac{\partial \bar{\psi}}{\partial \bar{r}} = 0 \quad \frac{\partial \bar{u}}{\partial \bar{r}} = 0 \quad \bar{v} = 0 \quad \frac{\partial \bar{\phi}}{\partial \bar{r}} = 0 \quad (5-6d)$$

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At the capillary wall ($\bar{r} = 1$),

$$\bar{\psi} = \bar{\zeta} \quad \bar{u} = 0 \quad \bar{v} = 0 \quad \frac{\partial \bar{\phi}}{\partial r} = 0.0 \quad (5-6e)$$

The dimensionless conjugate governing equation for heat conduction in the capillary wall is expressed as

$$\frac{\partial \bar{T}}{\partial \bar{t}} = \frac{1}{\text{Pr Re}} \left[\frac{1}{\bar{r}} \frac{\partial}{\partial \bar{r}} \left(\bar{r} \bar{k}_s \frac{\partial \bar{T}}{\partial \bar{r}} \right) + \frac{\partial}{\partial \bar{z}} \left(\bar{k}_s \frac{\partial \bar{T}}{\partial \bar{z}} \right) \right] \quad (5-7a)$$

The third-kind of temperature boundary condition is assumed at the outer channel wall,

$$-\bar{k}_s \frac{\partial \bar{T}}{\partial \bar{r}} \bigg|_{\bar{r}=1+\Delta/R} = \frac{h R}{k_{ref}} (\bar{T} - 1) \quad (5-7b)$$

5.2.6 Mass species transport equation

Consider a sample species to be transported between two reservoirs through a capillary as shown in Fig 5-1. Under the assumptions mentioned in chapter 2, the mass transport equation can be formulated as

$$\begin{aligned} \frac{\partial C_s}{\partial t} + (u + u_{ep}) \frac{\partial C_s}{\partial z} + (v + v_{ep}) \frac{\partial C_s}{\partial r} = \\ \frac{1}{r} \frac{\partial}{\partial r} \left[r D_s(T) \frac{\partial C_s}{\partial r} \right] + \frac{\partial}{\partial z} \left[D_s(T) \frac{\partial C_s}{\partial z} \right] \end{aligned} \quad (5-8a)$$

The dependence of the sample diffusivity $D_s(T)$ on T is assumed the same as that of $D_i(T)$ given in Eq. (4-18). u_{ep} and v_{ep} are the components of the electrophoretic velocity along axial and radial direction, respectively. Conceptually, the electrophoretic velocity refers to the motion of charged species in response to an

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applied electric field, and it is zero for neutral species. Generally, they can be expressed as

$$u_{ep} = \mu_{ep} \times E_z \quad (5-8b)$$

$$v_{ep} = \nu_{ep} \times E_r \quad (5-8c)$$

where μ_{ep} and ν_{ep} are the components of the electrophoretic mobility in axial and radial direction, respectively. They can be described by the Stokes equation as

$$\mu_{ep} = \nu_{ep} = \frac{\sigma e}{6\pi\mu(T)r_s} \quad (5-8d)$$

According to Weast *et al.* (1986), the electrophoretic mobility of the species, can be simply expressed as

$$\mu_{ep} = \mu_{ep0} + 0.025\mu_{ep0}(T - 298) \quad (5-8e)$$

$$\nu_{ep} = \nu_{ep0} + 0.025\nu_{ep0}(T - 298) \quad (5-8f)$$

where μ_{ep0} and ν_{ep0} are the components of the electrophoretic mobility in x and y direction at room temperature (i.e. 298 K), respectively.

Introducing the dimensionless parameters,

$$\begin{aligned} \bar{C}_s &= \frac{C_s}{C_{sref}} & \bar{t}^* &= \frac{t}{R^2/\nu} & \bar{u}_{ep} &= \frac{u_{ep}}{U_{ref}} \\ \bar{\nu}_{ep} &= \frac{\nu_{ep}}{U_{ref}} & \bar{D}_s &= \frac{D_s(T)}{D_{sref}} & Sc &= \frac{\nu_{ref}}{D_{sref}} \end{aligned} \quad (5-9)$$

Then, Eq. (5-8) can be non-dimensionalized as

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$$\frac{\partial \bar{C}_s}{\partial \bar{t}^*} + \text{Re}(\bar{u} + \bar{u}_{ep}) \frac{\partial \bar{C}_i}{\partial \bar{z}} + \text{Re}(\bar{v} + \bar{v}_{ep}) \frac{\partial \bar{C}_s}{\partial \bar{r}} = \frac{1}{Sc} \left[\frac{1}{\bar{r}} \frac{\partial}{\partial \bar{r}} \left(\bar{r} \bar{D}_s \frac{\partial \bar{C}_s}{\partial \bar{r}} \right) + \frac{\partial}{\partial \bar{z}} \left(\bar{D}_s \frac{\partial \bar{C}_s}{\partial \bar{z}} \right) \right] \quad (5-10)$$

where C_{sref} and D_{sref} are the reference concentration and the mass diffusivity of the sample species, respectively. Generally C_{sref} is taken to be the initial concentration of the sample species, i.e. C_0 , and D_{sref} is taken to be the mass diffusivity of the sample species at room temperature, i.e. D_{s0} at 298K. Sc is the Schmidt number. For the sample species transport, two cases are considered: in case I, the sample species is continuously supplied from the reservoir at the inlet, namely the translating interface; and case II is concerned with a certain amount of the sample species injected from the inlet for a short duration only and then dispersed as solution flows, namely the dispersion of a finite sample plug. Both cases are described by the mass transport equation (i.e. Eq. (5-10)) together with the following initial and boundary conditions

Initial conditions, $t = 0$

$$\text{Case I: } C_s = 0.0 \quad \text{Case II: } \begin{cases} C_s = C_0 & (z \leq l_0) \\ C_s = 0.0 & (z > l_0) \end{cases} \quad (5-11a)$$

For $t > 0$, boundary conditions

$$\text{Inlet:} \quad \text{Case I: } C_s = C_0 \quad \text{Case II: } C_s = 0.0 \quad (5-11b)$$

$$\text{Outlet:} \quad \frac{\partial C_s}{\partial z} = 0 \quad (5-11c)$$

$$\text{Centerline:} \quad \frac{\partial C_s}{\partial r} = 0 \quad \text{Capillary wall:} \quad \frac{\partial C_s}{\partial r} = 0 \quad (5-11d)$$

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It should be pointed out here that in case II, the injected sample plug length is assumed as 2 % of the capillary length ($l_0 = 0.02L$). In fact, this value is arbitrarily selected. The choice of such initial condition is to facilitate numerical computation. Strictly speaking, the more rigorous initial condition should be taken to be $C_s = \frac{m_s}{A} \delta(z)$ (here m_s is the injected sample mass, A is the capillary cross-sectional area, and $\delta(z)$ is the mathematical Dirac function). As such, it can be shown as a controlled sample mass by $\int_{-\infty}^{+\infty} C_s A dz = \int_{-\infty}^{+\infty} \frac{m_s}{A} \delta(z) A dz = m_s$.

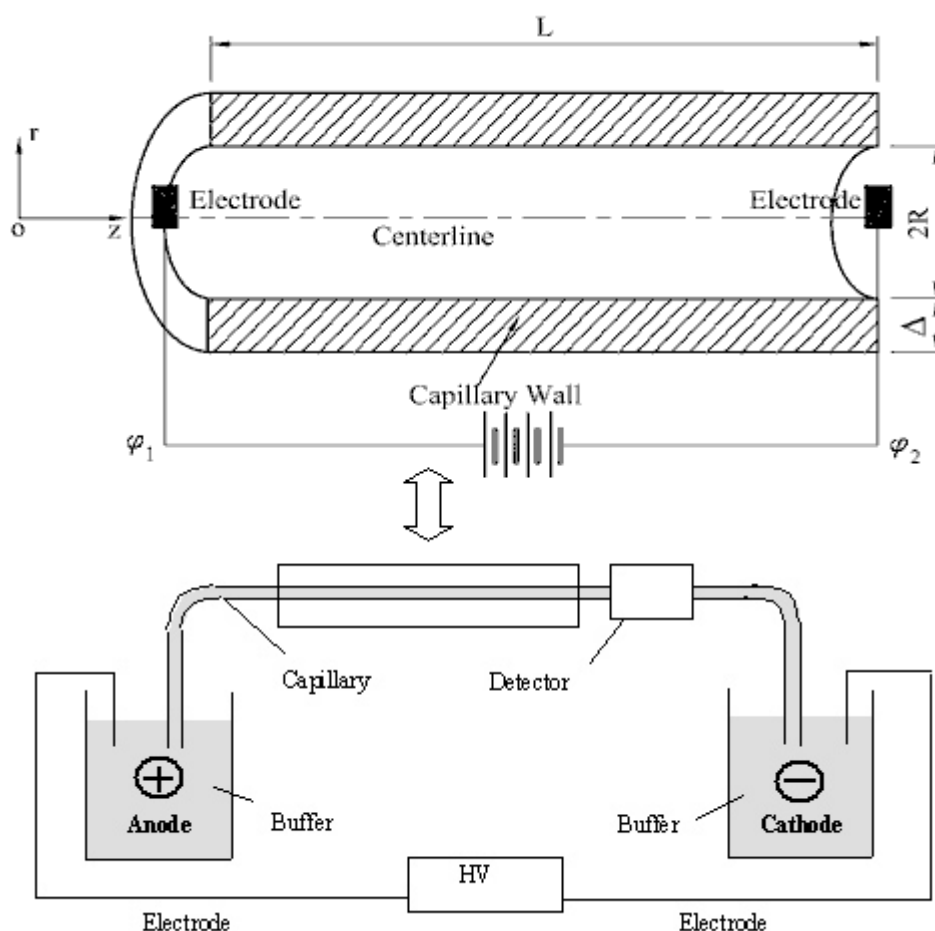


Fig. 5-1 Schematic diagram of the capillary electrophoresis system and focused computation domain

5.3 Validation and comparison of the numerical schemes

The numerical schemes for evaluating the Joule heating and its effect on the EOF have been validated in chapter 4. In this chapter, both the Crank-Nicolson and the Power-law numerical schemes for the mass transport equation are validated by comparing the numerical results with the analytical solutions which are available in the absence of Joule heating. As pointed out in chapter 4, without Joule heating effects, it is unnecessary to include the energy equation in the mathematical models, and all phenomenological coefficients can be taken to be constant. Thus, using the cross-sectional averaging method, the transient electrokinetic mass transport equation becomes one-dimensional, and can be further expressed in terms of the cross-sectional average of the sample concentration, the EOF velocity, and the effective mass diffusivity (accounting for the effect of the Taylor-Aris dispersion (*Probstein*, 1994)). Then using the Laplace transformation, a closed-form solution for this one-dimensional advection-dispersion equation can be obtained analytically for the simple case of the translating interface, that is, the sample species is continuously injected from the inlet reservoir by electrokinetic transport.

5.3.1 Validation of numerical schemes

For a fully developed electroosmotic flow without Joule heating effects, $v = 0$ and $E_r = 0$. Thus, Eq. (5-8) can be simplified to

$$\frac{\partial C_s}{\partial t} + (u + u_{ep}) \frac{\partial C_s}{\partial z} = D_{s0} \frac{\partial^2 C_s}{\partial z^2} + \frac{D_{s0}}{r} \frac{\partial}{\partial r} \left(r \frac{\partial C_s}{\partial r} \right) \quad (5-12)$$

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where according to Eq. (4-29), the dimensional EOF velocity is given by

$$u = -\frac{\varepsilon_0 \varepsilon_r E_z \zeta}{\mu} \left(1 - \frac{\psi}{\zeta}\right), \quad \text{and the electrophoretic velocity is expressed as}$$

$$u_{ep} = \mu_{ep0} E_z = \text{const}.$$

Applying the cross-sectional averaging method to Eq. (5-12) by using

$$\phi^* = \frac{2}{R^2} \int_0^R \phi r dr \quad (\text{here } \phi \text{ is the variable to be averaged, e.g., } C_s, u \text{ and } u_{ep}), \quad \text{Eq. (5-12)}$$

can be rewritten as

$$\frac{\partial C_s^*}{\partial t} + (u^* + u_{ep}^*) \frac{\partial C_s^*}{\partial z} = D_{eff} \frac{\partial^2 C_s^*}{\partial z^2} \quad (5-13)$$

where the C_s^* , u^* and u_{ep}^* respectively denote the cross-sectional average of the ample concentration, the EOF velocity, and the electrophoretic velocity. D_{eff} is the effective mass diffusivity accounting for the mass diffusion coefficient (D_{s0}) and the diffusion due to the Taylor-Aris dispersion (D_T), i.e. $D_{eff} = D_{s0} + D_T$. Generally, for the pressure-driven flow, since the convective velocity of the solute is lower near the walls than it is in the center, an initially focused band of solute will spread out as convection proceeds in the axial direction. Ultimately, this convective spreading process is limited by diffusion across streamlines, known as Taylor dispersion. For the pressure driven flow, the diffusion due to Taylor dispersion can attain the value of several to ten times as that due to the molecular mass diffusion. Therefore, Dutta and Leighton (2001, 2002, 2003a, 2003b) recently have focused on the reduction of Taylor's dispersion in pressure driven flow by optimizing the channel geometry. For the electrokinetic flow, without Joule heating effects, due to the “plug-like” velocity, the EOF allows sample transport with little dispersion (Dutta and Leighton, 2002). In

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addition, for the cases in this section (i.e. $E = 100V/cm$ ($u \approx 0.5mm$), $R = 50\mu m$, $D = 2.0 \times 10^{-10} m^2/s$), the channel length scale (i.e. $L = 50mm$) is much larger than the entrance length for Taylor dispersion, which according to Dutta and Leighton (2001), is defined as the diffusion time across the channel multiplied to the velocity, or the solutal Peclet number times the channel dimension (i.e. $uR^2/D \approx 7.5mm$). Thus, the analysis of the diffusivity due to the Taylor dispersion in this section is valid. While for the rest case studies in this thesis (i.e., $E = 500V/cm$ ($u \approx 3.0mm$), $R = 50 \sim 100\mu m$, $D = 2.0 \times 10^{-10} m^2/s$), the entrance length for Taylor dispersion is in the same order as the length of the channel (i.e., $L \approx O(uR^2/D)$). In other words, the sample processing time concerned in this thesis is in the same order as the time required for the solute molecules to diffuse across the channel width (i.e., $t \approx O(R^2/D)$). Therefore, the analytical solutions for diffusivity due to the Taylor dispersion (2001) is not valid. Consequently, the full numerical simulation of the sample transport and dispersion is needed. Under the Debye-Hückel approximation, it can be shown that the expression for the diffusivity due to the Taylor-Aris dispersion (D_T) is (see in Appendix E)

$$D_T = \frac{U_0^2}{D_{s0}} \left[\left(\frac{1}{2\kappa^2} + \frac{4}{R^2\kappa^4} \right) \frac{I_1(\kappa R)^2}{I_0(\kappa R)^2} - \frac{1}{\kappa^2} + \frac{2}{\kappa^3 R} \frac{I_1(\kappa R) I_2(\kappa R)}{I_0(\kappa R)^2} + \frac{1}{\kappa^2} \frac{I_1(\kappa R) I_3(\kappa R)}{I_0(\kappa R)^2} \right] \quad (5-14)$$

where I_2 is the first kind, second order modified Bessel function, and I_3 is the first kind, the third order modified Bessel function.

The initial and boundary conditions corresponding to the case of the translating interface are specified as

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$$\text{At } t = 0 \quad C_s = 0 \quad (5-15a)$$

$$\text{At } z = 0 \quad C_s = C_0 \quad \text{At } z = L \quad \frac{\partial C_s}{\partial z} = 0 \quad (5-15b)$$

Using the Laplace transformation, it can be shown that an analytical solution to Eq. (5-13) subjected to its initial and boundary conditions for the translating interface given in Eqs. (5-15a & b) can be given by

$$C_s^* = \frac{C_0}{2} \left\{ \operatorname{erfc} \left[\frac{z - (u^* + u_{ep}^*)t}{2\sqrt{D_{eff}t}} \right] + \exp \left[\frac{(u^* + u_{ep}^*)z}{D_{eff}} \right] \operatorname{erfc} \left[\frac{z + (u^* + u_{ep}^*)t}{2\sqrt{D_{eff}t}} \right] \right\} \quad (5-16)$$

where $\operatorname{erfc}(x) = \frac{2}{\sqrt{\pi}} \int_x^\infty e^{-\eta^2} d\eta$ is the complementary error function.

For the translating interface, namely on the basis of the boundary conditions specified in Eqs. (5-15a & b), in the absence of Joule heating effects numerical computations are carried out by solving the governing Eq. (5-12). A comparison between the numerical results and the analytical solutions is shown in Fig. 5-2 for axial variation of the cross-sectional average of the sample concentration. As for the demonstration of no Joule heating effects, dilute solution concentration $n_0 = 6.022 \times 10^{-20} \text{ m}^{-3}$ (i.e., $C_0 = 10^{-6} \text{ M}$) and low applied electric voltages $\varphi_1 = 500 \text{ V}$ and $\varphi_2 = 0 \text{ V}$ (i.e., $E_z = 100 \text{ V/cm}$) are chosen in the calculation. Although Eq. (5-14) indicates that the diffusivity due to Taylor dispersion scales as the square of the Peclet number. However, for the cases concerned in this section (no Joule heating), i.e. $C = 10^{-6} \text{ M}$, $R = 50 \text{ }\mu\text{m}$, $T = 298 \text{ K}$, $\varepsilon_r = 78.5$, $\mu = 0.9 \times 10^{-3} \text{ Pa}\cdot\text{s}$, $\rho = 998 \text{ kg/m}^3$, $\zeta = -50 \text{ mV}$, $E_z = 100 \text{ V/cm}$ and $D = 2.01 \times 10^{-10} \text{ m}^2/\text{s}$ (for uncaged fluorescein dye), using Eq. (5-14), we can obtain

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the ratio of the diffusivity due to Taylor's dispersion to the mass diffusion coefficient, that is $D_T / D_{s0} = 1.5 \times 10^{-2}$. Therefore, the diffusivity due to Taylor-dispersion can be neglected as compared to the mass diffusivity in this situation. As such, the sample "diffusion zone" in the following cases is mainly determined by the mass diffusion rather than by the Taylor dispersion. It is shown in Fig. 5-2 that the numerical results of the Crank-Nicolson scheme are nearly the same as the analytical solutions for the sample species concentration distributions. However, a discrepancy is observed between the numerical results of the Power-law scheme and the analytical solutions. Such a deviation is attributed to the so-called numerical pseudo diffusion. The detailed discussion of the cause and the resolution of the numerical pseudo diffusion can be found in *Patankar* (1980). Because of very low diffusion coefficient of the sample species (e.g., $D_0 \approx 10^{-10} \text{ m}^2/\text{s}$), the sample species transport equation is classified as a convection-dominant equation. For such kind of convection-dominant equation, the Power-law scheme reduces to first-order. Consequently, it leads to higher numerical pseudo diffusion, and hence results in the unrealistic mass transport results as shown in Fig. 5-2.

5.3.2 Comparison of the numerical schemes

To compare and discuss the two numerical schemes used for the mass transport equation, computations have been carried out for cases without considering the Joule heating effects. Instead the characteristic length (e.g. the channel dimension) based Peclet number, it is the grid size based Peclet number which has a strong impact on the magnitude of the numerical pseudo diffusion. However, given a channel size and spatial grids, there is a one-to-one correlation between the characteristic length based Peclet number and the grid size based Peclet number. Therefore, the channel length

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based Peclet number is still chosen as a parameter to discuss the numerical pseudo diffusion. As earlier discussed, the diffusivity due to Taylor-dispersion can be neglected as compare with the mass diffusion coefficient. Hence the channel length based Peclet number is changed by solely varying sample mass diffusivity from $2.01 \times 10^{-9} m^2/s$ (equivalent to $P_e = 5$) to $2.01 \times 10^{-10} m^2/s$ ($P_e = 50$) and $2.01 \times 10^{-11} m^2/s$ ($P_e = 500$) in this study.

Moreover, as mentioned earlier, for the sample species transport, two cases are considered in the calculation, Case I, the translating interface; and Case II, the dispersion of a finite sample plug.

5.3.2.1 Translating interface

The variation of the cross-sectional average sample mass concentrations along the axial direction and time evolution of sample species concentrations in a capillary for Peclet number $P_e = 50$ is shown in Fig. 5-3a and 5-3b. Because of the very low diffusion coefficient of sample species (i.e., $D_0 \approx O(10^{-10}) m^2/s$), we can estimate that the characteristic length based Peclet number is of order 10^2 , suggesting that the species transport is dominated by convection and mainly transported with the flow. For the convection-dominated transport with such high Peclet numbers, the Power-law scheme reduces to the first-order accuracy and tends to give rise to higher numerical pseudo diffusion, especially in the region of large concentration gradient. It can be seen from Fig. 5-3 that the length of the diffusion region obtained from the Power-law scheme is larger than that from the Crank-Nicolson scheme and this difference is seen to extend along the capillary as the time elapses. This is due to the factor that the Power-law scheme gives rise to larger numerical pseudo diffusion, resulting in unrealistic mass transport results.

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Since the Peclet number is the most important parameter characterizing the sample species electrokinetic transport, the results obtained from the two numerical schemes for different Peclet numbers are compared. The time evolution of sample species concentrations in a capillary for three Peclet numbers (i.e., 5, 50, 500) is shown in Fig. 5-4. Physically, the Peclet number represents the ratio of shear forces to Brownian forces, or, the ratio of convection to diffusion. For example, keeping other conditions unchanged, an increase in the Peclet number indicates stronger convection or weaker diffusion. As a result, the diffusion region should be decreased. While as shown in the Fig. 5-4, when the Peclet number is larger than 50, the Power-law scheme seems to generate the same diffusion region for the different Peclet numbers (i.e. 50, 500). Definitely, this is not the physical situation and the diffusion is numerically enlarged because of the numerical pseudo diffusion. Fig. 5-4 also demonstrates that the Crank-Nicolson scheme can give the reasonable results, namely, keeping other parameters unchanged, the diffusion region decreases with increasing Peclet number.

5.3.2.2 Dispersion of a finite sample plug

In most capillary electrophoresis applications, the sample is injected as a plug, and then the sample plug moves with the flow downstream for analysis. In order to concentrate the sample zone and improve the sensitivity of analysis, it is necessary for the samples to be manipulated into a narrow band.

Figure 5-5a and 5-5b respectively give the variation of the cross-sectional average sample mass concentrations along the axial direction and the time evolution of sample concentrations for case II, the dispersion of a finite sample plug in a capillary ($P_e = 50$). It is well known that since the total mass of the sample is

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conserved during the transport, the area underneath every “pulse” remains invariant. As a result, the effect of the diffusion causes to broaden the sample band and thus lower sample peak as shown in Fig. 5-5. It is shown that compared to the Crank-Nicolson scheme, the Power-law scheme numerically enlarges the diffusion significantly. Fig. 5-6 presents the evolution of the mass concentrations for case II, the dispersion of a finite sample plug with three Peclet numbers (i.e. 5, 50, 500). As mentioned earlier, the Peclet number physically represents the ratio of convection to diffusion. Therefore the physically realistic scenario is that if keeping the convection unchanged, larger Peclet number indicates weaker diffusion and hence leads to smaller diffusion region. However, it is noted from Fig. 5-6 that when the Peclet increases from 50 to 500, the decrease of diffusion region obtained from the Power-law scheme is undistinguished. This can be attributed to the numerical pseudo diffusion induced by the Power-law scheme. While further observing Fig. 5-6, it can be seen that when the Peclet number increases from 5 to 50 and 500, the decrease of the diffusion region can be clearly observed. This suggests that the Crank-Nicolson scheme can provide the reasonable results for the simulation of electrokinetic mass transport in microchannels.

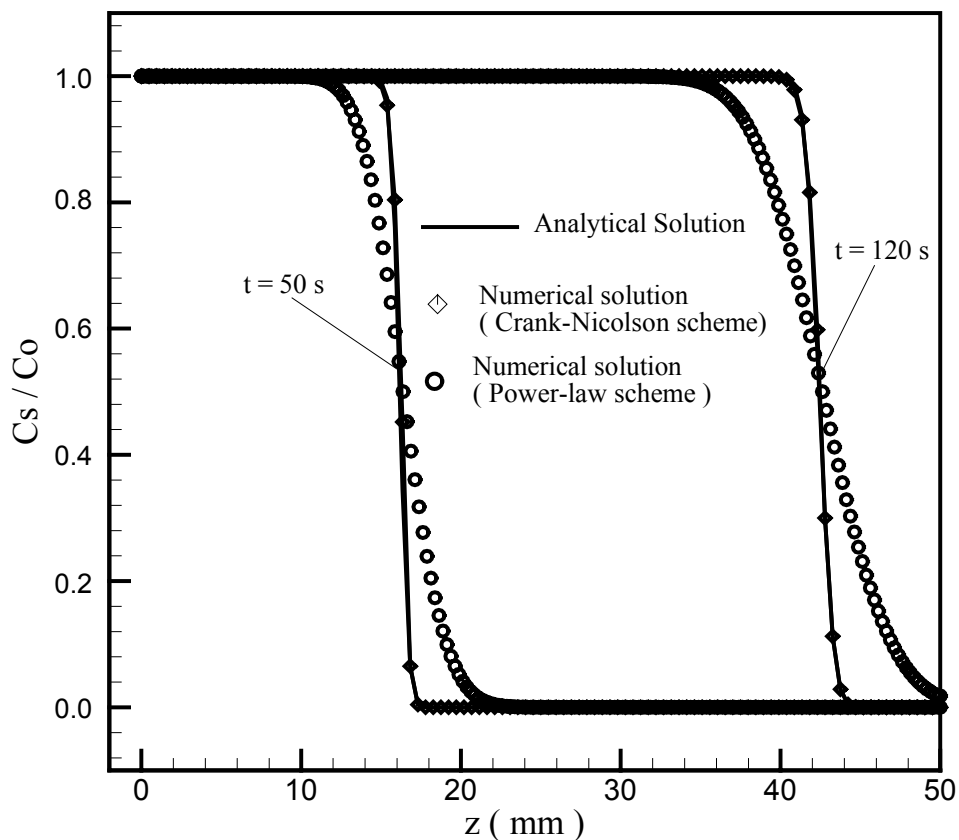
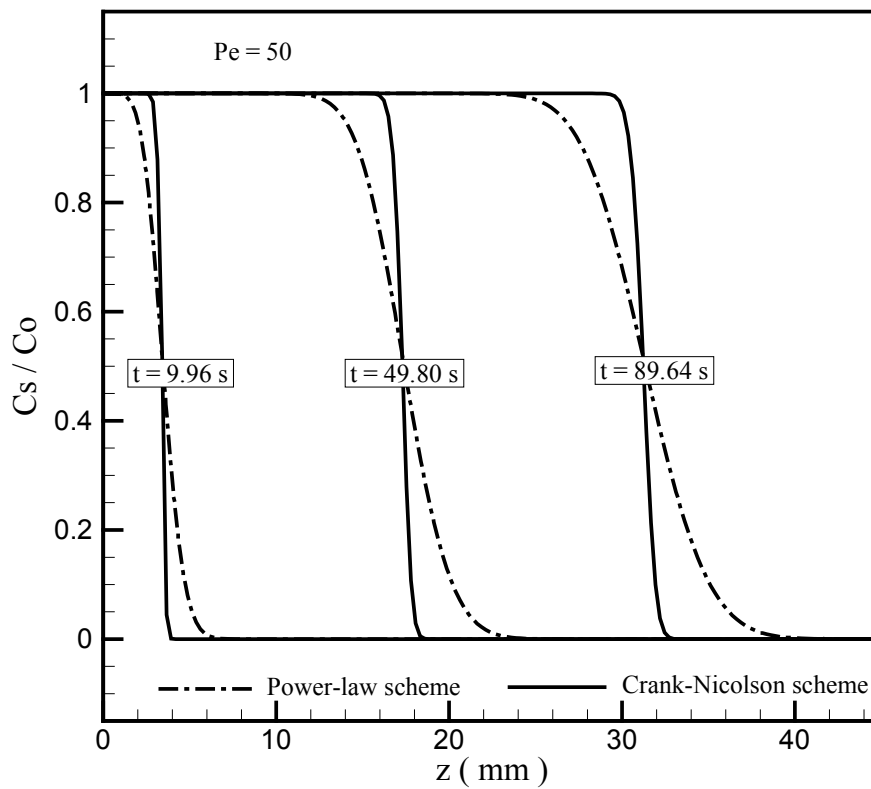


Fig. 5-2 Comparison of the numerical results of axial variation of the cross-sectional average of the sample concentration obtained from the Power-law scheme and the Crank-Nicolson scheme with the analytical solutions for Case I, the translating interface, namely the sample species is continuously injected from the inlet reservoir by electrokinetic transport.

The parameters are: $R = 50 \mu m$, $\phi_1 = 500V$, $\phi_2 = 0V$, $C = 10^{-6} M$, $\zeta = -50mV$, $D = 2.01 \times 10^{-10} m^2/s$ and $\mu_{ep0} = 0 m^2/V \cdot s$.



(a)

Fig. 5-3 Comparison of the sample species concentration distributions between the Power-law scheme and the Crank-Nicolson scheme for Case I, the translating interface: (a) the sample mean concentrations at different times varying along the axial direction.

The parameters are: $R = 50 \mu m$, $\varphi_1 = 500V$, $\varphi_2 = 0V$, $C = 10^{-6} M$, $\zeta = -50mV$, $D = 2.01 \times 10^{-10} m^2 / s$ and $\mu_{ep0} = 0 m^2 / V \cdot s$.

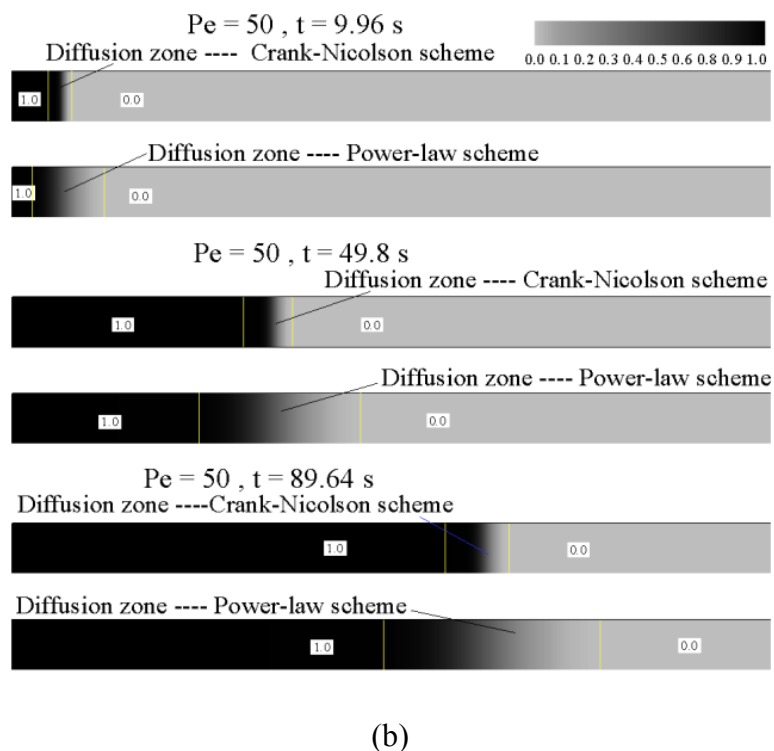


Fig. 5-3 Comparison of the sample species concentration distributions between the Power-law scheme and the Crank-Nicolson scheme for Case I, the translating interface: (b) time evolution of the sample species concentration distributions in the capillary

The parameters are: $R = 50 \mu m$, $\varphi_1 = 500V$, $\varphi_2 = 0V$, $C = 10^{-6} M$, $\zeta = -50mV$, $D = 2.01 \times 10^{-10} m^2 / s$ and $\mu_{ep0} = 0 m^2 / V \cdot s$.

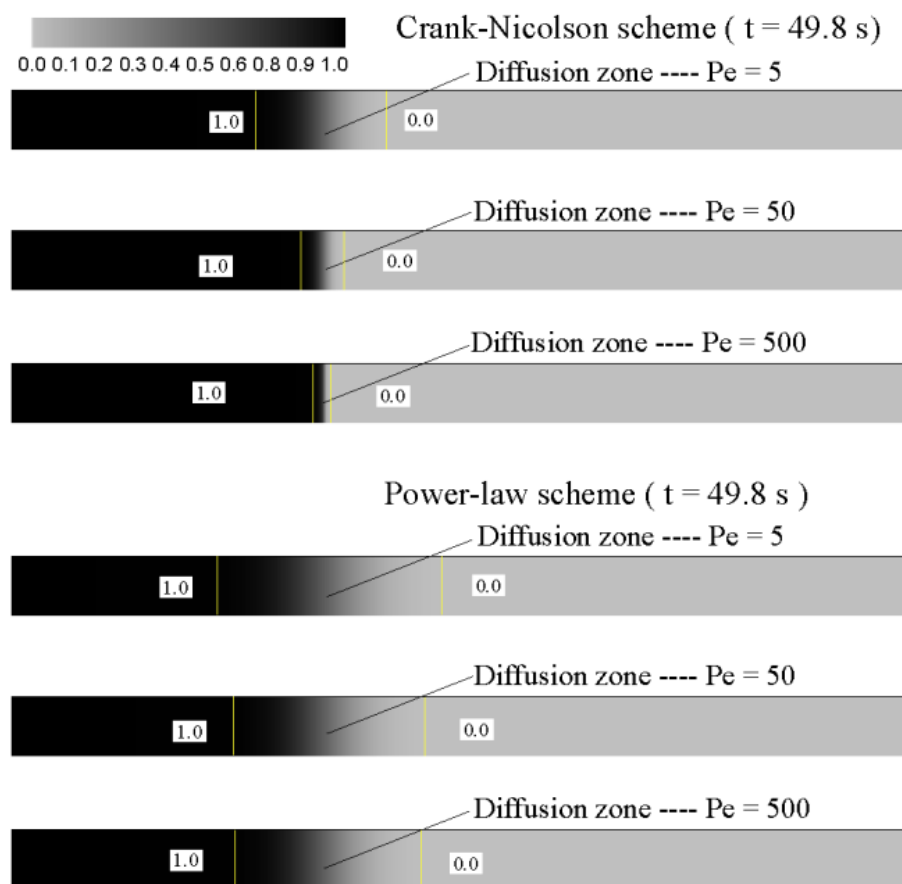
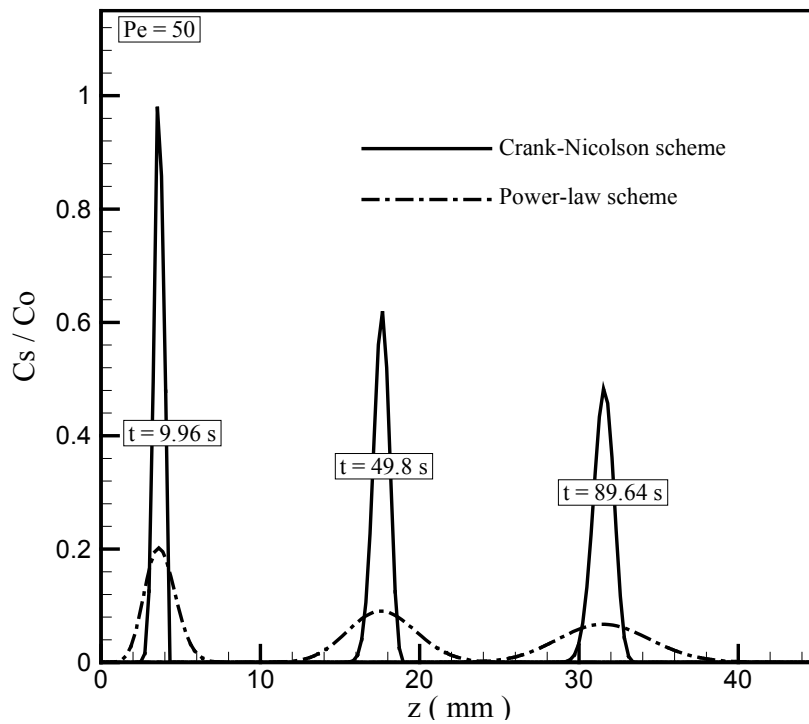


Fig. 5-4 Time evolution of sample species concentration obtained from the Power-law scheme and the Crank-Nicolson scheme for Case I, the translating interface with three Peclet numbers (5, 50, 500).

The parameters are: $R = 50 \mu m$, $\varphi_1 = 500V$, $\varphi_2 = 0V$, $C = 10^{-6} M$, $\zeta = -50mV$ and $\mu_{ep0} = 0 m^2 / V \cdot s$.

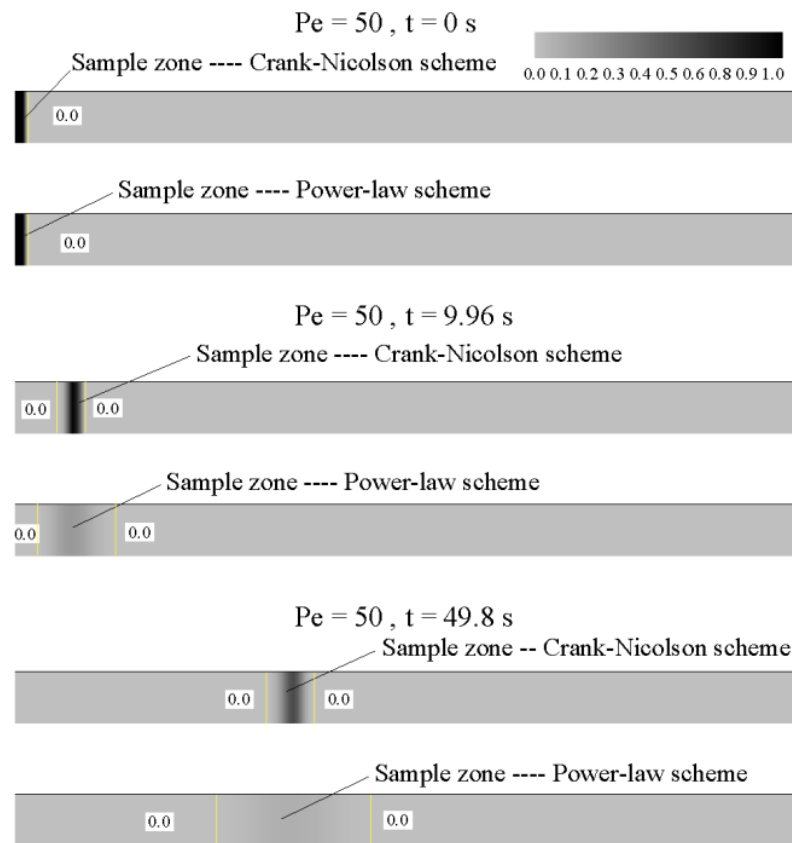


(a)

Fig. 5-5 Comparison of the sample species concentration distributions between the Power-law scheme and the Crank-Nicolson scheme for Case II, the dispersion of a finite sample plug: (a) the sample mean concentrations at different times varying along the axial direction.

The parameters are: $R = 50 \mu m$, $\varphi_1 = 500V$, $\varphi_2 = 0V$, $C = 10^{-6} M$, $\zeta = -50mV$, $D = 2.01 \times 10^{-10} m^2 / s$ and $\mu_{ep0} = 0 m^2 / V \cdot s$.

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(b)

Fig. 5-5 Comparison of the sample species concentration distributions between the Power-law scheme and the Crank-Nicolson scheme for Case II, the dispersion of a finite sample plug: (b) time evolution of the sample species concentration distributions in the capillary.

The parameters are: $R = 50 \mu m$, $\varphi_1 = 500V$, $\varphi_2 = 0V$, $C = 10^{-6} M$, $\zeta = -50mV$, $D = 2.01 \times 10^{-10} m^2 / s$ and $\mu_{ep0} = 0 m^2 / V \cdot s$.

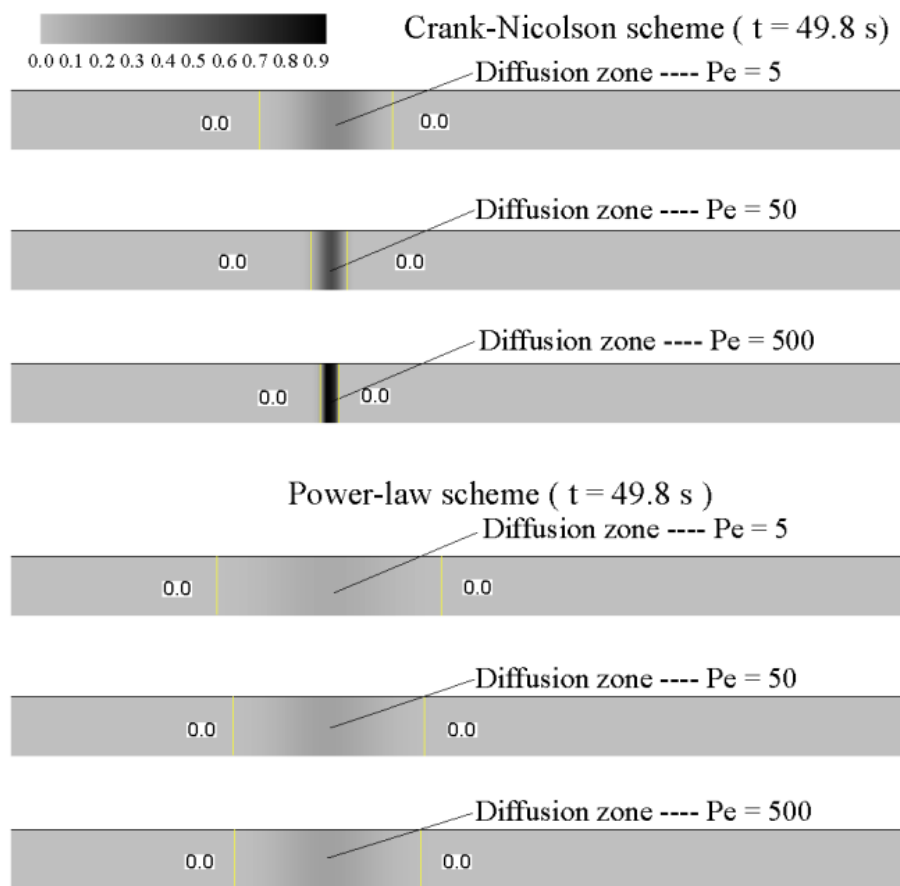


Fig. 5-6 Time evolution of sample species concentration obtained from the Power-law scheme and the Crank-Nicolson scheme for Case II, the dispersion of a finite sample plug with three Peclet numbers (5, 50, 500).

The parameters are: $R = 50 \mu m$, $\varphi_1 = 500V$, $\varphi_2 = 0V$, $C = 10^{-6} M$, $\zeta = -50mV$, and $\mu_{ep0} = 0 m^2 / V \cdot s$.

5.4 Transient Joule heating and its effects

As pointed out in previous sections, the Joule heat induced temperature development during electrokinetic mass transport can influence a myriad of

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phenomena between the mobile and stationary phase. As such, the thermal characteristics of electrokinetic mass transport offer a fertile source of information about the fundamental mechanisms that lead to optimized performance. In this section, the Joule heating induced transient temperature development and its effects on the *EOF* are discussed. Based on the conclusion drawn in the previous section, the results presented in this section are obtained using the Boltzmann distribution.

5.4.1 Temperature development

Figs. 5-7a and 5-7b respectively show the time evaluation of the axial mean temperature profiles and the radial temperature distributions of a liquid solution in a capillary with the following parameters: capillary inner radius $R = 100\mu m$, applied electric field $E = 500 V/cm$, bulk concentration $C = 0.1 M$, zeta potential $\zeta = -50 mV$, and heat transfer coefficient outside the capillary wall $h = 10 kW/m^2K$. The development of solution temperature due to the Joule heating in both thermal developing and developed regions is clearly demonstrated in these two figures. It is found that the solution temperature starts at the room temperature at the entrance, and achieves a fully developed temperature after 3 to 5 radii distance along the axial direction. Interestingly, the thermal entrance region (or developing length) is independent of time. Furthermore, the results show the time for the temperature field to attain the steady state is very short at the inlet, and then gradually increases in the thermal developing region. In the thermal developed region, the Joule heating starts to heat up the liquid solution very fast at initial stage. Subsequently the solution temperature gradually increases as the time elapses, and finally reached its steady state at 300 ms after the electric field is set up.

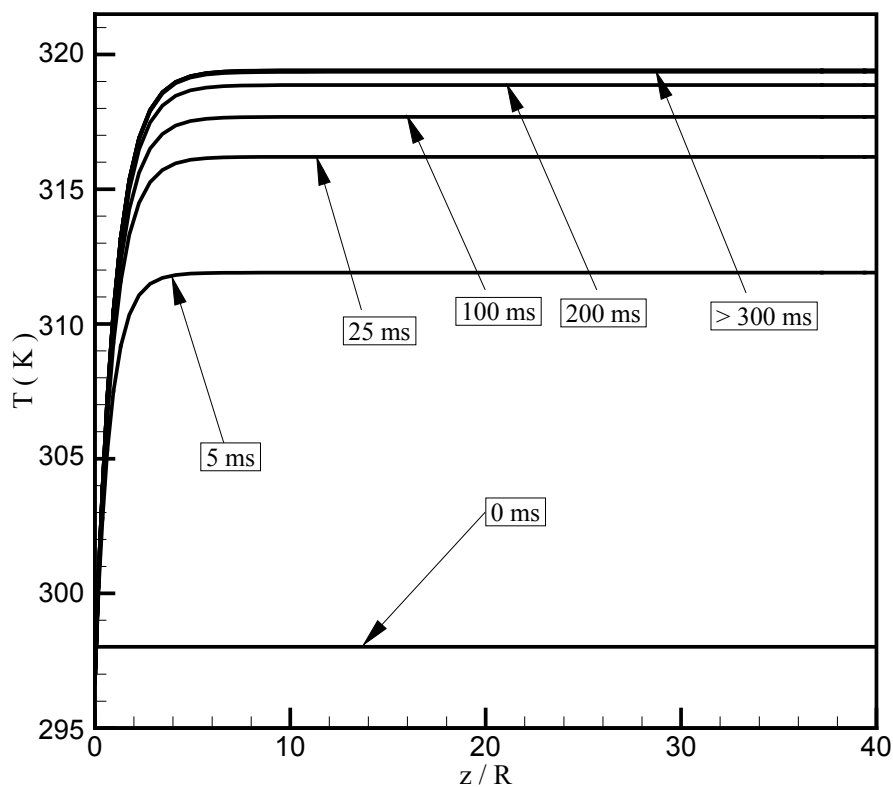
5.4.2 Transient electroosmotic flow velocity

Fig. 5-8 shows the transient dimensionless velocity distributions of the *EOF* in both the developing and the developed regions. As a comparison, the *EOF* velocity without Joule heating is shown by the dotted lines. According to Kang *et al.* (2002), without Joule heating effect the *EOF* can attain its steady state instantly upon imposing electric field (the characteristic time for the *EOF* to reach its steady state is estimated as $t_{cr} = R^2 / \nu = 5 \text{ ms}$ in this case), and because of large κR the dimensionless *EOF* velocity approaches the Smoluchowski velocity. With consideration of the Joule heating effect, however it is found that the time for the *EOF* to reach its steady state significantly increases to 300 ms. It is also interesting to note that the *EOF* development time is almost the same as that of the temperature field development (as shown in Figs 5-7a and 5-7b). This suggests that the change of the velocity distributions is mainly caused by the change of solution temperature resulted from the Joule heating, and the *EOF* field becomes strongly coupled with the Joule heating induced temperature field. The influence of temperature on the *EOF* velocity is attributed to the dependence of solution viscosity on temperature. Therefore, under the Joule heating effect, increment of the solution temperature causes a decrease in solution viscosity and dielectric constant, and hence results in the dimensionless *EOF* velocity larger than the reference Smoluchowski velocity.

Taking a close examination of the steady-state ($t > 300 \text{ s}$) radial velocity distributions shown in Fig. 5-8, it is found that due to large κR , the entrance effect on the *EOF* velocity distributions under no Joule heating effect is indiscernible. In contrast, the velocity distributions with Joule heating effect in the developing and the fully developed regions exhibit very differently. The results show that the velocity

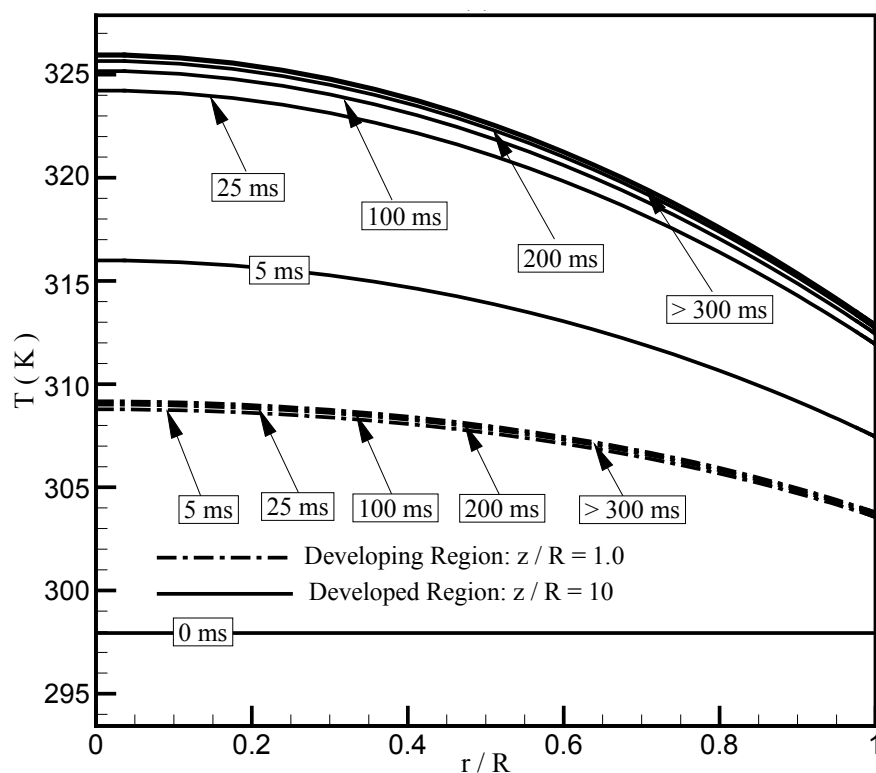
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distribution has a concave shape in the developing region, while with the flow advance it becomes flat, and eventually reaches convex pattern in the developed region. This scenario can be explained as follows. Because of the Joule heating, the solution mean temperature rises along the channel as shown in Fig. 5-7a. Such temperature gradient along the axial direction will induce the viscosity gradient and electric field strength gradient along the channel, and hence cause the velocity to vary along the flow direction. On the other hand, in order to maintain the flow rate conservation along the flow direction, an inner pressure gradient is induced along the flow direction in the channel as shown in Fig. 5-9, which presents the variation of the pressure along the axial direction. It can be found from Fig. 5-9 that there exist a small negative pressure gradient in the developing region and a positive pressure gradient in the fully developed region. Such inner pressure gradient would produce a “drag” effect (i.e., an adverse pressure gradient) on the developing flow and accordingly a “suction” effect (i.e., an favorable pressure gradient) to the developed flow. In the literature, the effect of favorable pressure gradient and adverse pressure gradient on EOF was discussed in length by *Santiago* (2001).



(a)

Fig. 5-7 Temporal and spatial developments of the Joule heating induced solution temperature field in a microcapillary, (a) variation of the mean temperature along the axial direction. The parameters used in this computation are: $R = 100 \mu m$, $E_0 = 500 V/cm$, $C = 10^{-1} M$, $\zeta = -50 mV$, and $h = 10 kW/m^2 K$.



(b)

Fig. 5-7 Temporal and spatial developments of the Joule heating induced solution temperature field in a microcapillary, (b) radial temperature distributions in both the developing and the developed regions. The parameters used in this computation are: $R = 100 \mu\text{m}$, $E_0 = 500 \text{V/cm}$, $C = 10^{-1} \text{M}$, $\zeta = -50 \text{mV}$, and $h = 10 \text{kW/m}^2 \text{K}$.

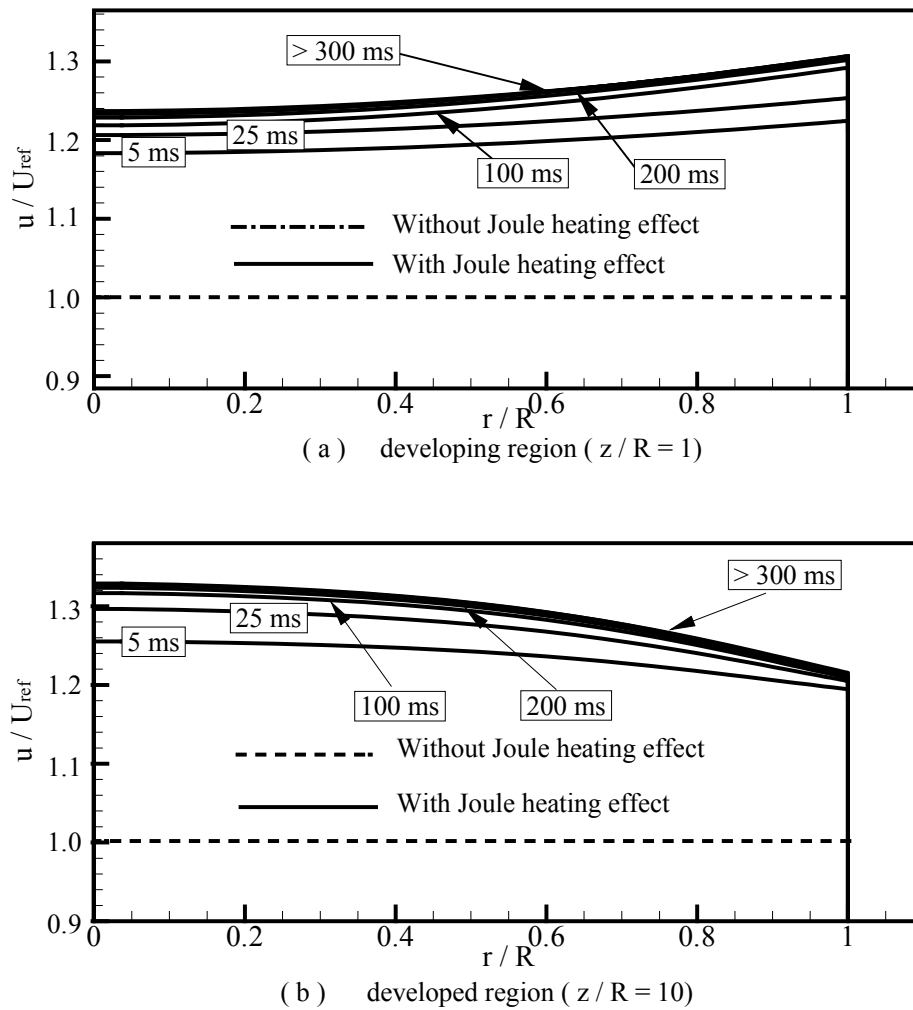


Fig. 5-8 Time evolution of the EOF velocity radial distributions in (a) the developing region and (b) the fully developed region with/without Joule heating effect. The parameters used in the computation are $R = 100 \mu m$, $E_0 = 500 V/cm$, $C = 10^{-1} M$, $\zeta = -50 mV$, and $h = 10 k W/m^2 K$.

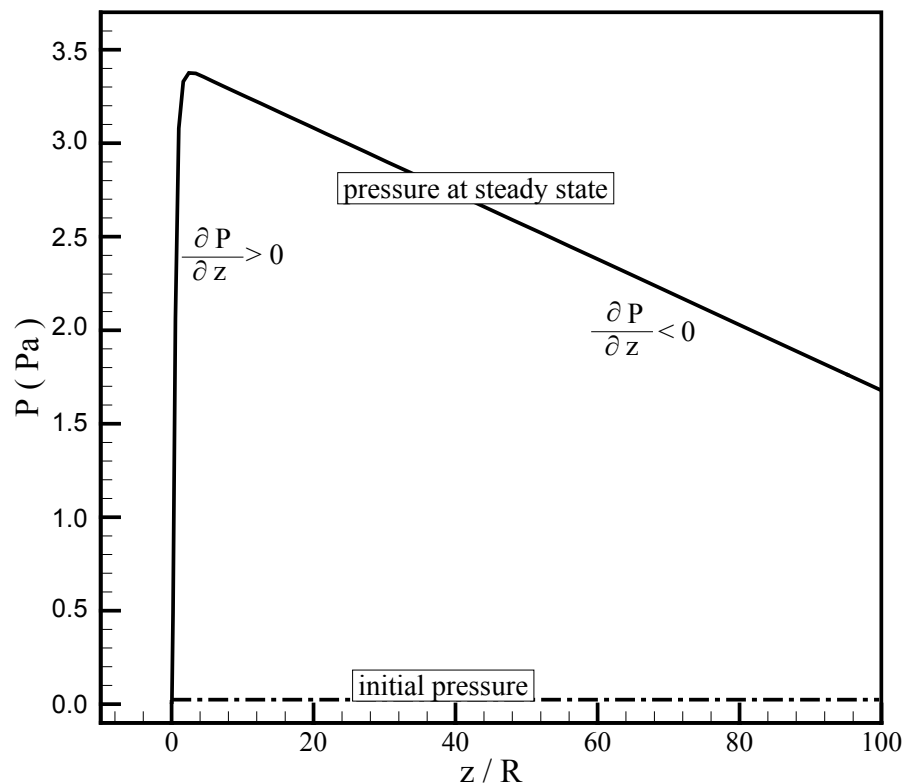


Fig. 5-9 Variation of the pressure profiles along the axial direction. The parameters used in the computation are $R = 100\mu m$, $E_0 = 500V/cm$, $C = 10^{-1}M$, $\zeta = -50mV$, and $h = 10kW/m^2 K$.

5.5 Steady state Joule heating and its effects

In this section, the steady-state Joule heating and the effects of the capillary size, the electrolyte concentration, the applied electrical field strength, and the heat transfer coefficient outside capillary wall will be discussed.

In these computations, microcapillaries are considered to be made of silica glass and have a length of $L = 50 mm$ and different radii but a fixed wall thickness of $70\mu m$ (e.g., Polymicro Technologies, USA). The working fluid is NaCl solution whose properties are: density $\rho = 998kg/m^3$, electrical conductivity (at room

temperature 25°C) $\lambda_{+0} = 50.08 \times 10^{-4} \text{ m}^2 \text{ S} / \text{ mol}$ and $\lambda_{-0} = 76.31 \times 10^{-4} \text{ m}^2 \text{ S} / \text{ mol}$ (Weast *et al*, 1986). Parametric studies including capillary radius, solution concentration and zeta potential, applied electric field strength, and heat transfer coefficient are carried out to quantitatively examine the Joule heating effects on the electroosmotic flow and mass species transport.

5.5.1 Effect of the capillary size

The radial temperature distributions (in the thermal fully-developed regime) in the liquid solution and the solid capillary wall for three different capillary radii are shown in Fig.5-10a. It is seen that the temperature distributions in the liquid exhibit a parabolic-like pattern, supporting the assumptions made by *Grushka and co-authors* (1989). This also shows that the heating due to viscous dissipation is not important. However, the parabolic shape seems to vary from case to case, depending on parametric conditions. The highest temperature occurs at the capillary centerline; this suggests that the heat generated by Joule heating is transferred from the central region to the wall by convection, and then dissipated through the capillary wall by conduction. Further, under the same physicochemical conditions, $E_0 = 500 \text{ V} / \text{ cm}$, $C = 0.1 \text{ M}$, $\zeta = -50 \text{ mV}$, and $h = 10 \text{ kW} / \text{ m}^2 \text{ K}$, the temperatures of both the liquid solution and solid wall in a large capillary ($R = 200 \mu \text{ m}$) are significantly higher than those in a small capillary ($R = 50 \mu \text{ m}$). The same trend can also be observed in the plots of the axial bulk temperature profile of the liquid solution in capillaries shown in Fig. 5-10b. This scenario may be attributed to the fact that as the capillary size becomes larger, the surface area-to-volume ratio becomes smaller, leading to a lower ratio of the heat dissipation (measured by surface) to the Joule heat generation

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(defined by volume). However, from a practical design viewpoint, choice of small-sized capillaries may be problematic because the detection sensitivity will decrease and sample species adsorption is enhanced for small capillaries.

In addition, according to *Yang et al.* (2001), the hydrodynamic entrance length of electroosmotic flows is negligible due to very low Reynolds numbers. In the present study, the typical Reynolds number is about $Re = 0.1$, giving rise to the entrance regime of the hydrodynamic flow of about 1% of the capillary radius only (*Yang et al.*, 2001). However, the thermal entrance due to Joule heating in electroosmotic flow is quite significant (see Fig.5-10b). The thermal entrance length is approximately about ten times as large as the capillary radius.

Fig.5-11 shows the dimensionless fully-developed electroosmotic flow velocity distributions for three different capillary radii. As mentioned earlier, in all computations, the reference velocity is defined as $U_{ref} = (\epsilon_{ref} \epsilon_0 / \mu_{ref}) E \zeta$ unless specified otherwise. In the absence of Joule heating, the velocity profile is uniform throughout most of the capillary. The unity dimensionless velocity indicates that the maximum velocity is determined by the Smoluchowski velocity (*Probstein*, 1994), $U_s = [\epsilon(T) \epsilon_0 / \mu(T)] E \zeta$, and is independent of the capillary radius. While in the presence of Joule heating, as previously discussed, the fluid temperature increases with capillary size. This leads to lower liquid viscosity which in turn results in higher fluid velocity as shown in Fig.5-11. It is also observed that without Joule heating effects, the velocity reaches a maximum value near the capillary wall. This is expected because the driving force in an electroosmotic flow is due to the interplay between the applied electric field and the net electric charge density that only exists within the thin EDL regime close to the wall. The flow extended to the rest region of

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the capillary is passive, and is attributed to hydrodynamic shear stresses due to viscosity.

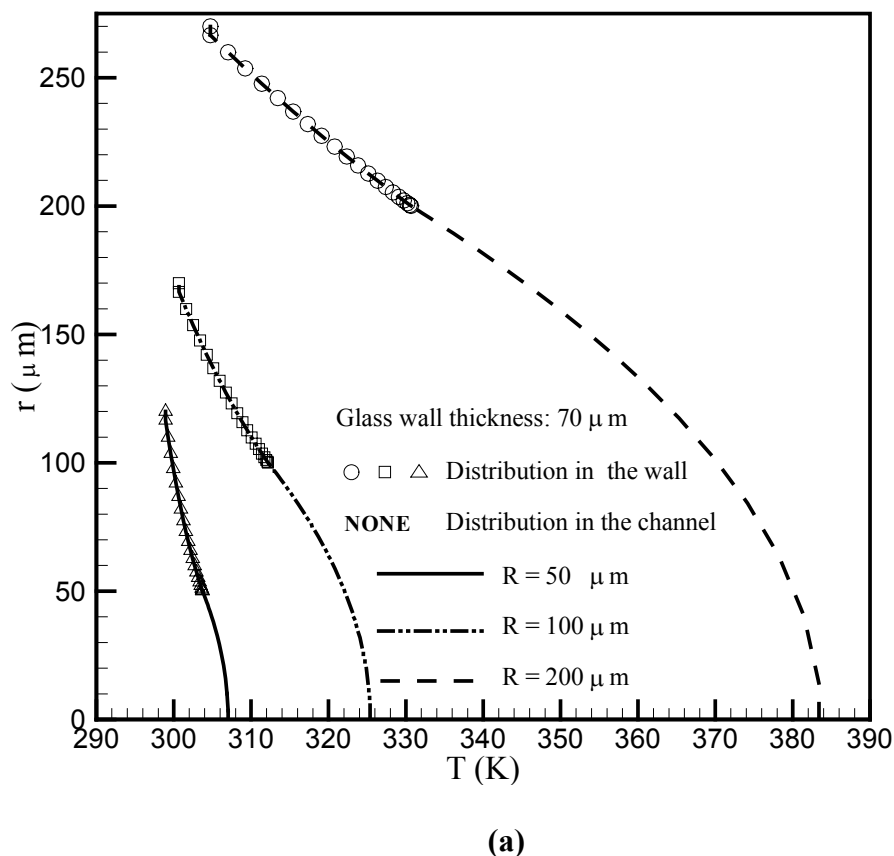
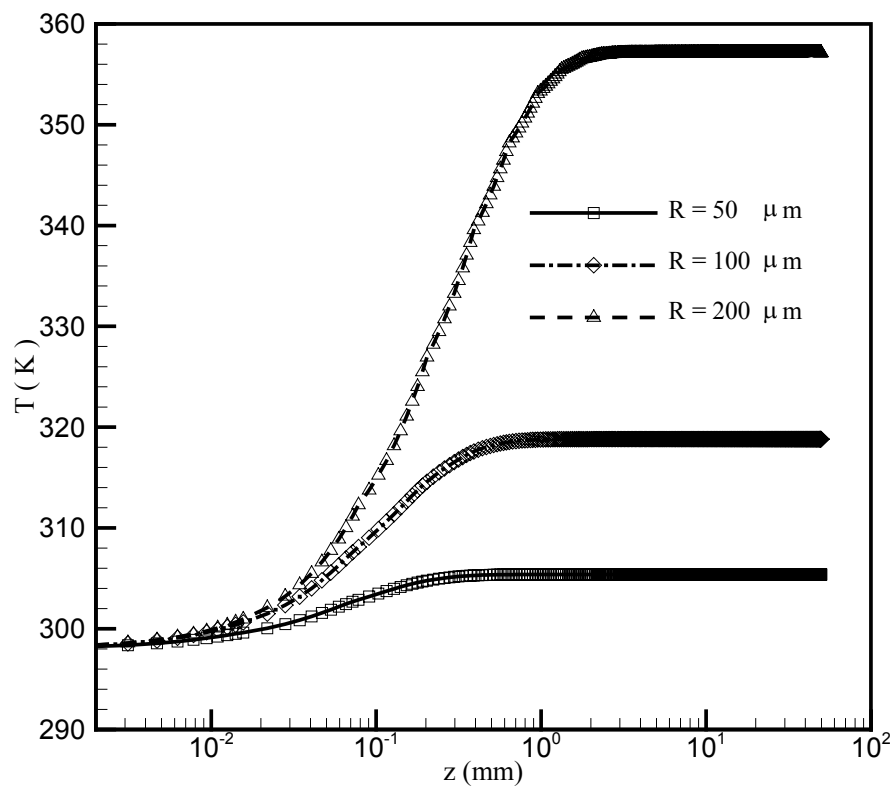


Fig. 5-10 Temperature distributions in the capillary for various capillary radii (wall thickness of $70 \mu\text{m}$), (a) radial temperature distributions in the capillary and its solid wall. Other parameters used in computations are $E_0 = 500 \text{ V/cm}$, $C = 10^{-1} \text{ M}$, $\zeta = -50 \text{ mV}$, and $h = 10 \text{ kW/m}^2 \text{ K}$.



(b)

Fig. 5-10 Temperature distributions in the capillary for various capillary radii (wall thickness of $70 \mu\text{m}$), (b) variation of solution mean temperature along the axial direction. Other parameters used in computations are $E_0 = 500\text{V/cm}$, $C = 10^{-1}\text{M}$, $\zeta = -50\text{mV}$, and $h = 10\text{kW/m}^2\text{K}$.

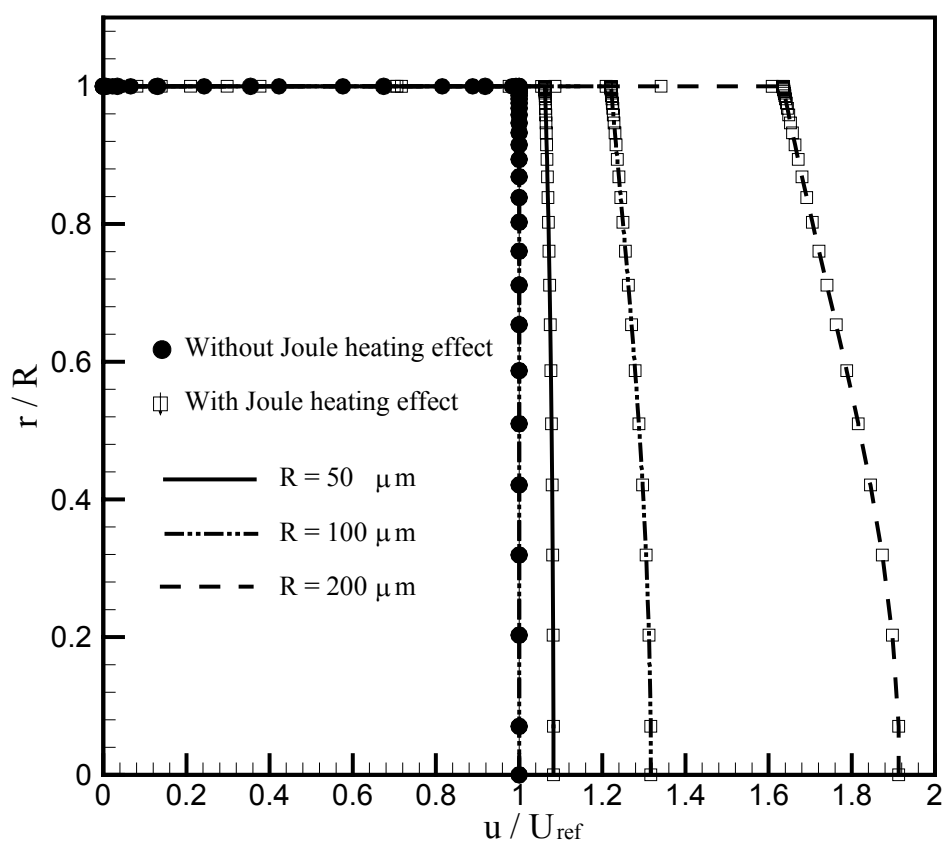
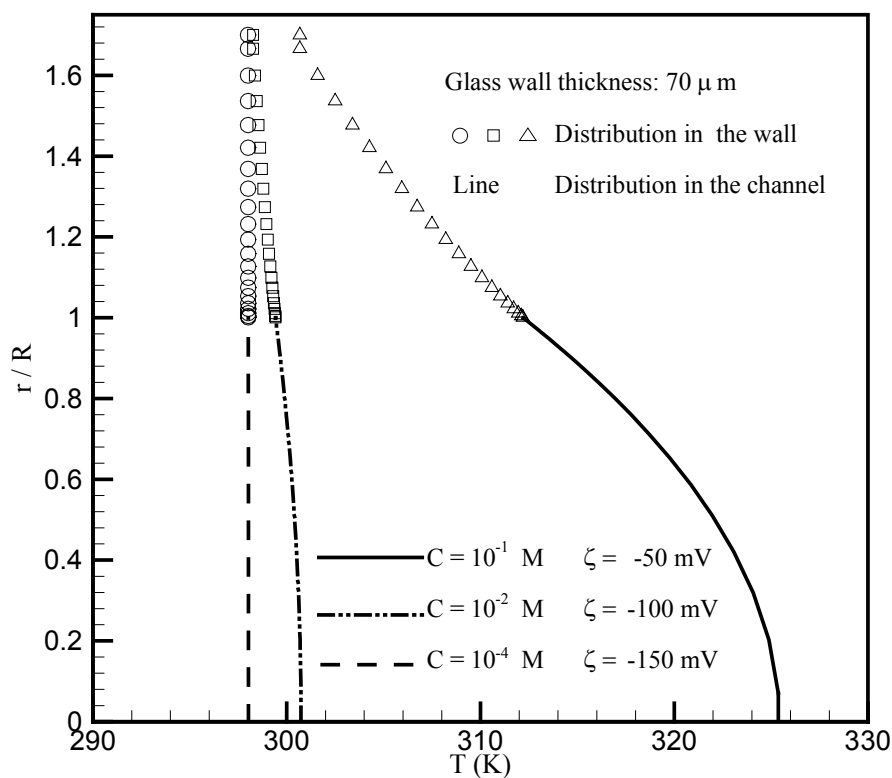


Fig. 5-11 Solution radial velocity distributions with/without Joule heating effects for different capillary radii (wall thickness of $70 \mu m$). Other parameters used in computations are $E_0 = 500 V/cm$, $C = 10^{-1} M$, $\zeta = -50 mV$, and $h = 10 kW/m^2 K$.

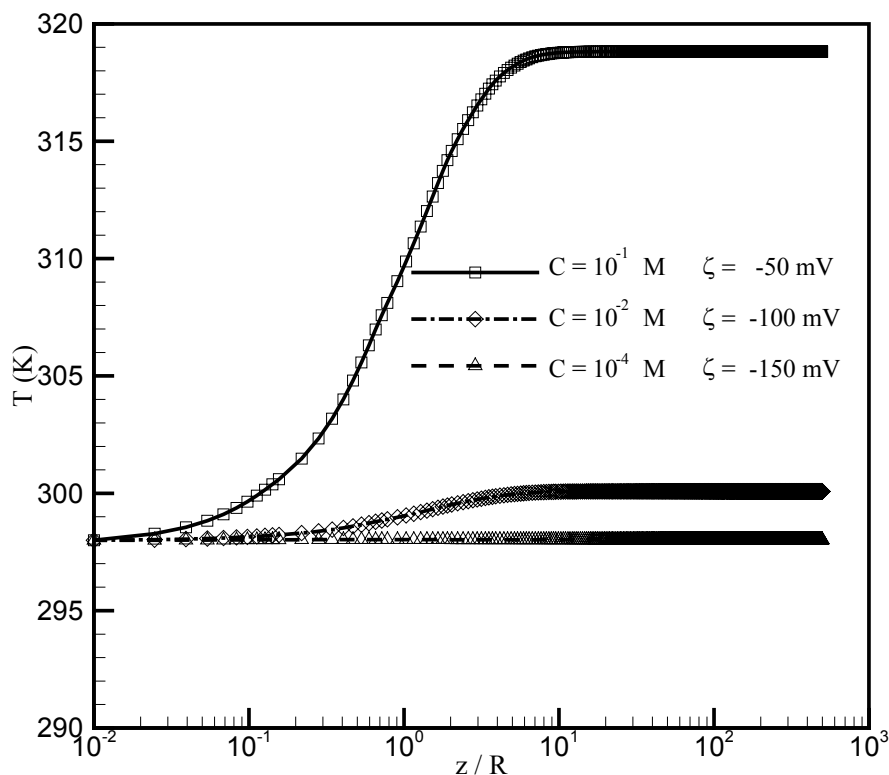
5.5.2 Effect of the electrolyte concentration

Fig.5-12a and Fig.5-12b present the radial temperature distributions and the axial bulk temperature profile in a capillary for three different solution concentrations, respectively. It is well-known that the capillary zeta potential is correlated to the solution concentration (*Hunter*, 1981). Hence, a variation of the zeta potentials is also included, and they are $C = 10^{-4} M$ ($\zeta = -150 mV$), $C = 10^{-2} M$ ($\zeta = -100 mV$), and $C = 10^{-1} M$ ($\zeta = -50 mV$). Other parameters are: $R = 100 \mu m$, $E_0 = 500 V/cm$, and $h = 10 kW/m^2 K$. According to Eq. (5-12), the heat generation due to Joule heating $\dot{q} = \lambda(T)E^2$ is associated with the liquid electrical conductivity, $\lambda(T)$, which in turn depends on the solution concentration. Hence, as expected, the solution temperature rise increases with increasing the solution concentration. This indicates that the Joule heating can be safely neglected for dilute solutions (e.g., $C = 10^{-4} M$). However, for solutions of high concentrations (e.g., $C = 10^{-1} M$), the Joule heating effect under parameters studied can lead to a $20^\circ C$ temperature increment, which has an impact on the electroosmotic flow velocity distributions (shown in Fig.5-13). From Fig.5-13, it can be seen that, due to large values of the electrokinetic radius, κR , the solution concentration itself has negligible effects on the dimensionless velocity distributions. However, as can be predicted from the Smoluchowski equation (*Probstein*, 1994), $U_s = [\frac{\epsilon(T)\epsilon_0}{\mu(T)}]E\zeta$, the magnitude of the velocity is proportional to the zeta potential, which is related to the solution concentration as mentioned earlier.



(a)

Fig. 5-12 Temperature distributions in the capillary for different combinations of the solution concentration and zeta potential, (a) radial temperature distributions in the capillary and its solid wall. Other parameters used in computations are $R = 100 \mu\text{m}$, $E_0 = 500 \text{ V/cm}$, and $h = 10 \text{ kW/m}^2 \text{ K}$.



(b)

Fig. 5-12 Temperature distributions in the capillary for different combinations of the solution concentration and zeta potential, (b) variation of solution mean temperature along the axial direction. Other parameters used in computations are $R = 100 \mu\text{m}$, $E_0 = 500 \text{ V/cm}$, and $h = 10 \text{ kW/m}^2 \text{ K}$.

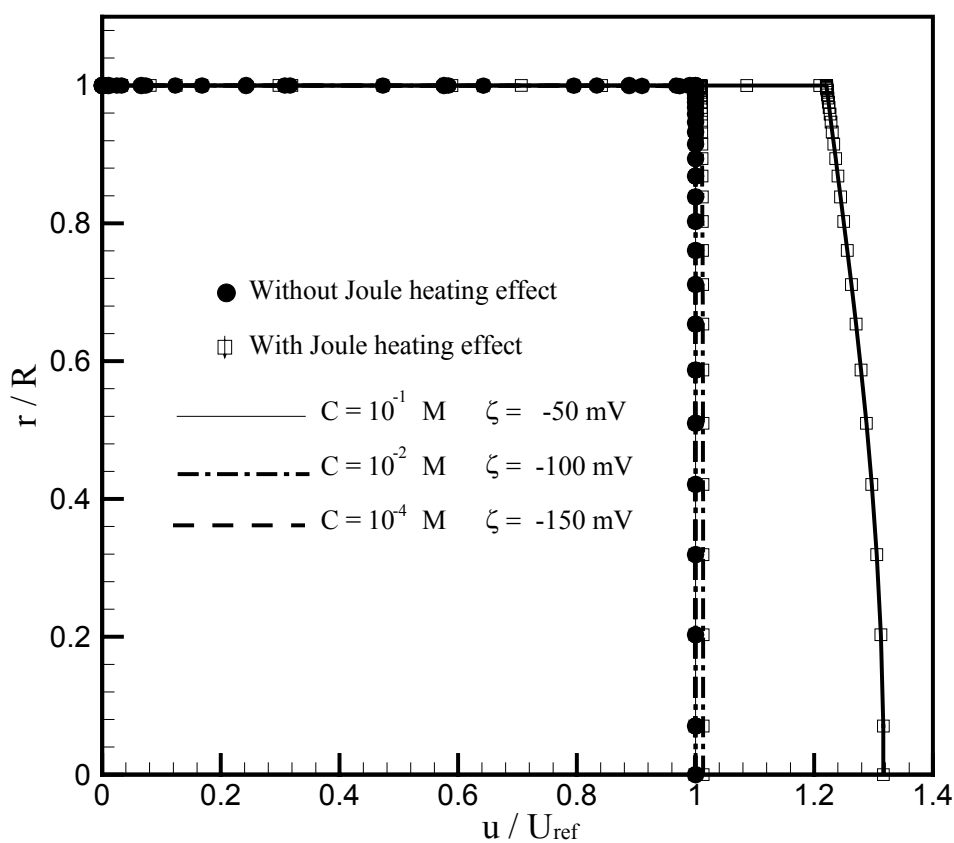
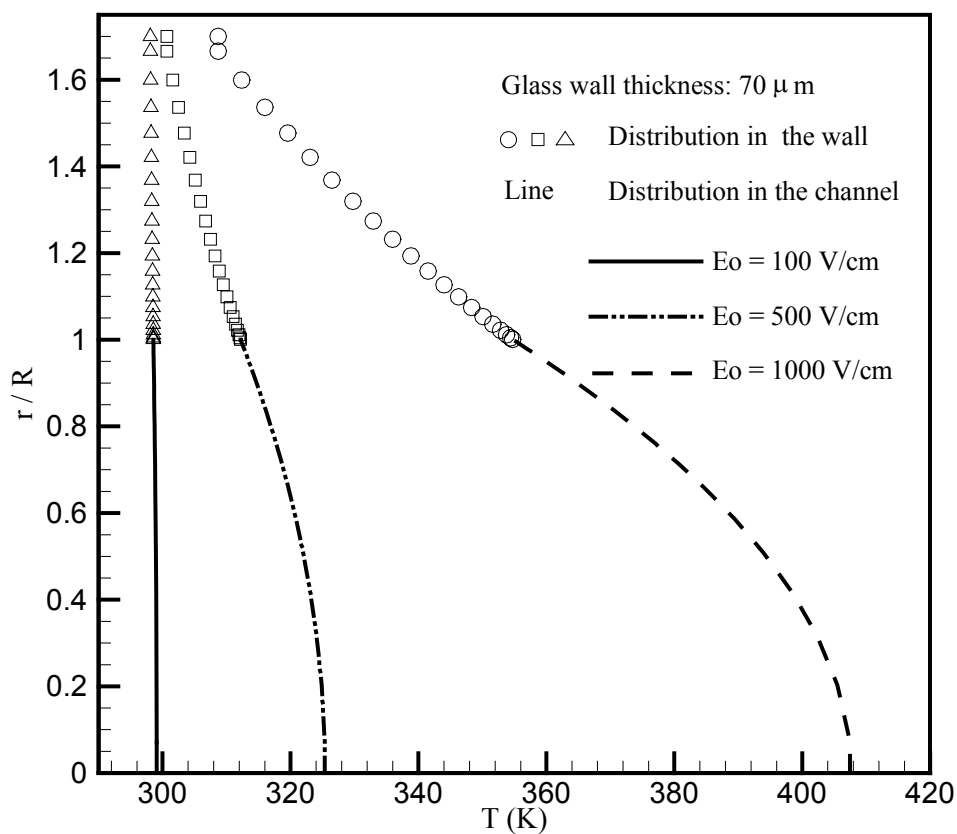


Fig. 5-13 Solution radial velocity distributions with/without Joule heating effects for different combinations of the solution concentration and zeta potential. Other parameters used in computations are $R = 100 \mu\text{m}$, $E_0 = 500 \text{ V/cm}$, and $h = 10 \text{ kW/m}^2 \text{ K}$.

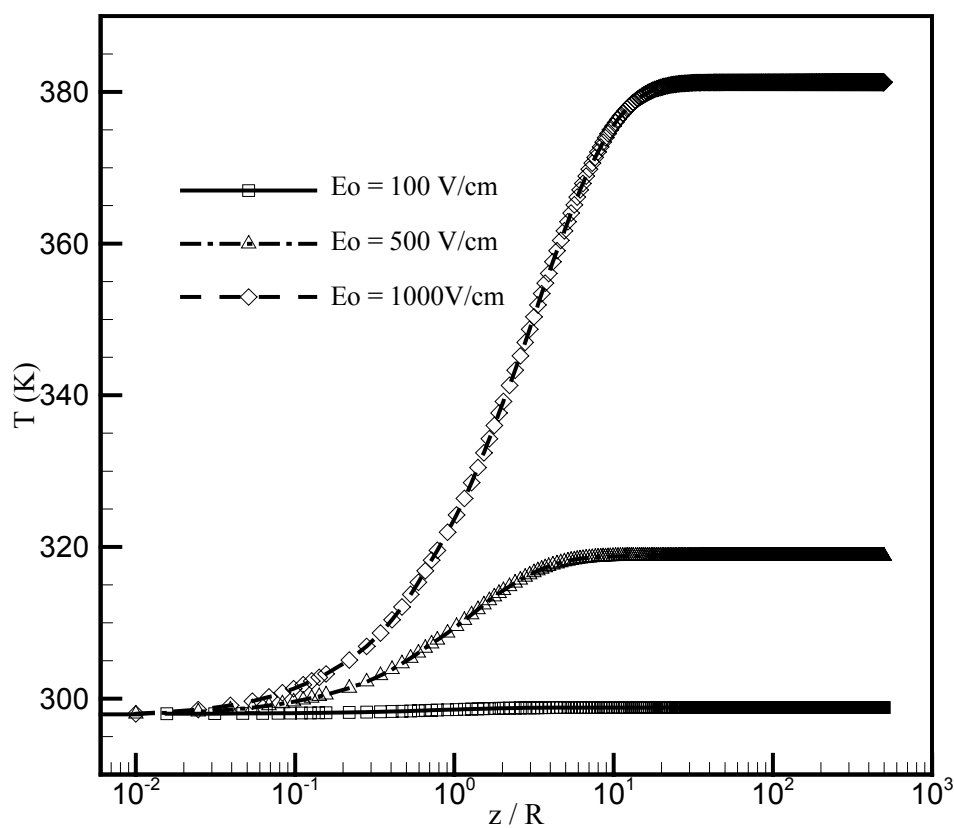
5.5.3 Effect of the applied electric field

As discussed earlier, According to Eq. (5-12a), the source term for Joule heating can be expressed as $\dot{q} \approx E^2 \lambda(T)$, this suggests that the Joule heating strongly depends on the applied electric field strength, E . The quantitative, supporting evidence is shown using the radial temperature distributions (Fig. 5-14a) and the axial mean temperature profile (Fig.5-14b) in a capillary for three different electric field strengths. Other parameters used in calculations are: $R = 100 \mu m$, $C = 0.1 M$, $\zeta = -50 mV$, and $h = 10 kW/m^2 K$. The results in Figs 5-14a and 5-14b show that for parameters considered, the Joule heating effect under low field strength is negligible (e.g., $E_0 = 100 V/cm$). Under high electric field strength, for instance $E_0 = 1000 V/cm$, the present single-phase model predicts that the solution temperature can increase up to above $100^\circ C$, and hence vapor bubbles could be generated. The experimental evidence of the presence of vapor bubbles under high electric fields was reported in the literature (Gobie and Cornelius, 1990). Fig.5-15 show the effects of applied electric field on electroosmotic flow velocity distributions. Similar to the capillary radius and zeta potential, a change of the field strength does not affect the non-dimensional velocity distribution if the Joule heating is not included. With Joule heating, the presence of temperature increment causes the velocity distribution to deviate from the normal situation.



(a)

Fig. 5-14 Temperature distributions in the capillary for different applied electric field strengths, (a) radial temperature distributions in the capillary and its solid wall. Other parameters used in computations are $R = 100 \mu\text{m}$, $C = 10^{-1} \text{ M}$, $\zeta = -50 \text{ mV}$, and $h = 10 \text{ kW/m}^2 \text{ K}$.



(b)

Fig. 5-14 Temperature distributions in the capillary for different applied electric field strengths, (b) variation of solution mean temperature along the axial direction. Other parameters used in computations are $R = 100 \mu m$, $C = 10^{-1} M$, $\zeta = -50 mV$, and $h = 10 kW/m^2 K$.

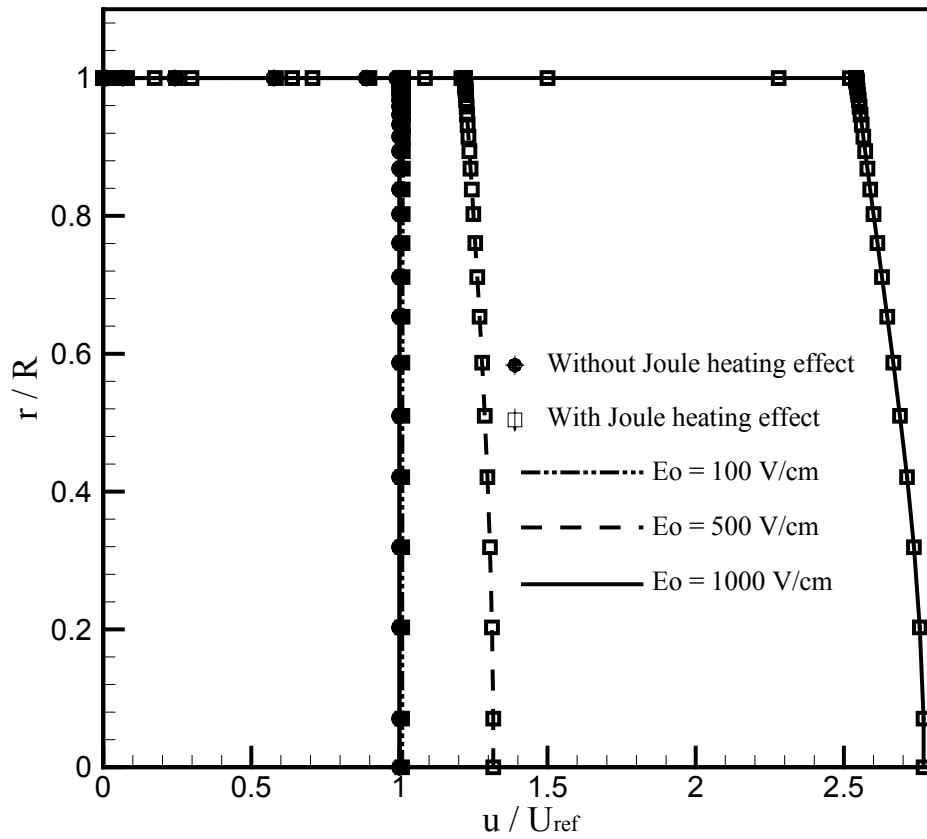
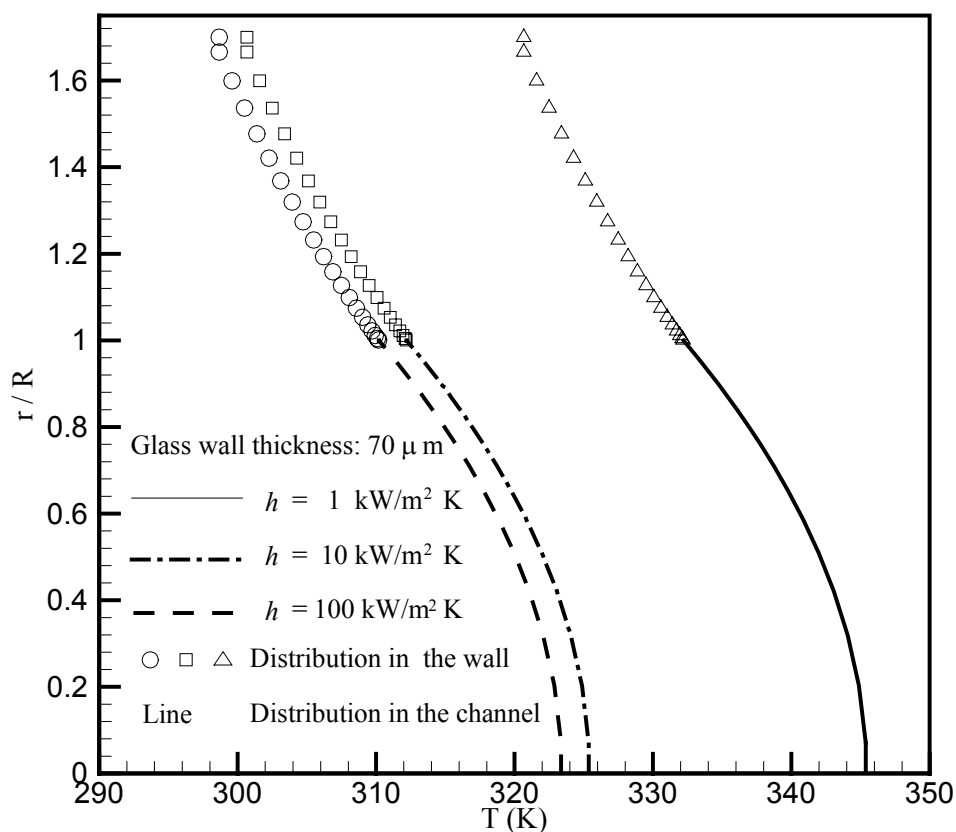


Fig. 5-15 Solution radial velocity distributions with/without Joule heating effects for different applied electric field strengths. Other parameters used in computations are $R = 100 \mu m$, $C = 10^{-1} M$, $\zeta = -50 mV$, and $h = 10 kW/m^2 K$.

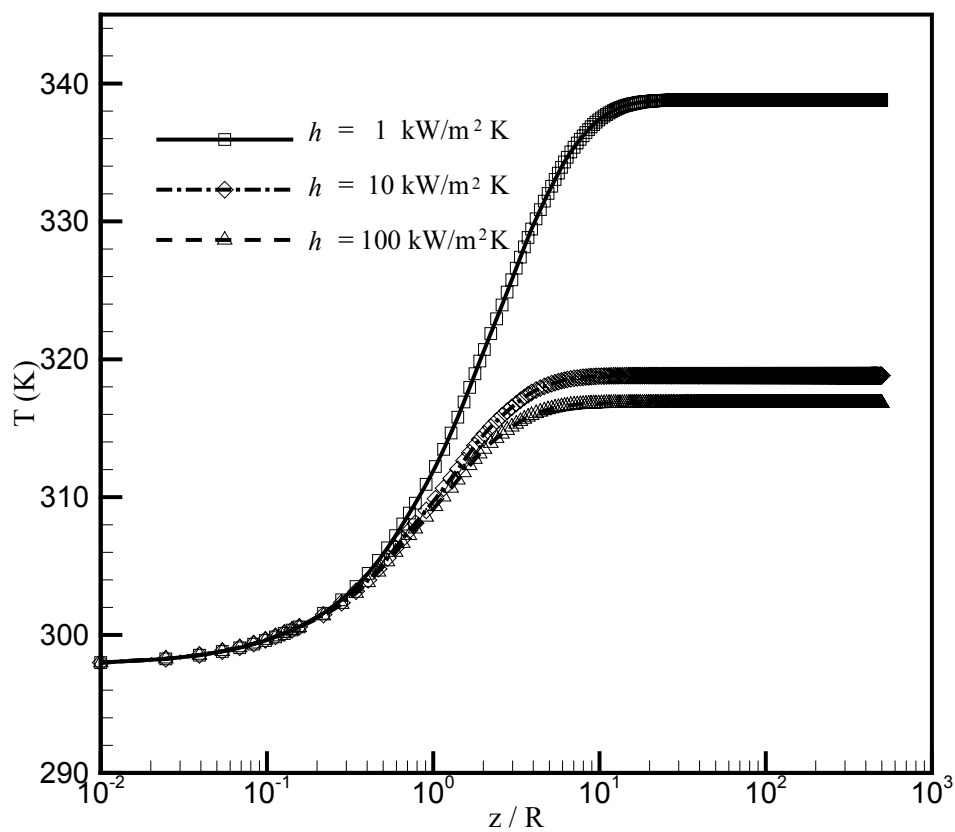
5.5.4 Effect of the heat transfer coefficient

The general approach minimizing Joule heating effects in a capillary electrophoresis system is to remove the heat by using different cooling systems. Therefore the effect of the heat transfer coefficient outside the capillary wall is investigated. In most commercial capillary electrophoresis systems, special cooling systems are employed to dissipate the heat effectively. The capillary is usually surrounded by low boiling point liquid in thermostated liquid bath (*Grushka, et al.*, 1989). For such a cooling system, the heating transfer coefficient outside the capillary generally can reach to the order of $10\text{ kW/m}^2\text{K}$ (*Grushka, et al.*, 1989, *Jones and Grushka*, 1989). For the calculations in this section, three different heat transfer coefficients are considered: $1\text{ kW/m}^2\text{K}$, $10\text{ kW/m}^2\text{K}$, and $100\text{ kW/m}^2\text{K}$, which in practice are respectively corresponding to the cooling systems with different conditions, such as different cooling liquids and different flush velocity (i.e. Reynolds number). Other parameters used in calculations are: $R = 100\text{ }\mu\text{m}$, $E_0 = 500\text{ V/cm}$, $C = 0.1\text{ M}$, and $\zeta = -50\text{ mV}$. The calculated radial temperature distributions and the axial bulk temperature profiles in a capillary under the influence of the heat transfer coefficient are given Fig. 5-16a and Fig. 5-16b, respectively. Interestingly, the shape of radial temperature distributions is almost the same, irrespective the heat transfer coefficient. Fig. 5-17 shows the electroosmotic flow velocity distributions along the axial direction. The results demonstrate that the choice of cooling system has a strong impact on the electroosmotic flow velocity in microcapillaries. It shows that the cooling mode with the high heat transfer coefficient $h = 100\text{ kW/m}^2\text{K}$ is the most effective means for heat removal and temperature control in the capillary electrophoresis.



(a)

Fig. 5-16 Temperature distributions in the capillary under influences of the heat transfer coefficient outside the capillary wall, (a) radial temperature distributions in the capillary and its solid wall. Other parameters used in computations are $R = 100 \mu\text{m}$, $C = 10^{-1} M$, $\zeta = -50 \text{ mV}$, and $E_0 = 500 \text{ V/cm}$.



(b)

Fig. 5-16 Temperature distributions in the capillary under influences of the heat transfer coefficient outside the capillary wall, (b) variation of solution mean temperature along the axial direction. Other parameters used in computations are $R = 100 \mu m$, $C = 10^{-1} M$, $\zeta = -50 mV$, and $E_0 = 500 V/cm$.

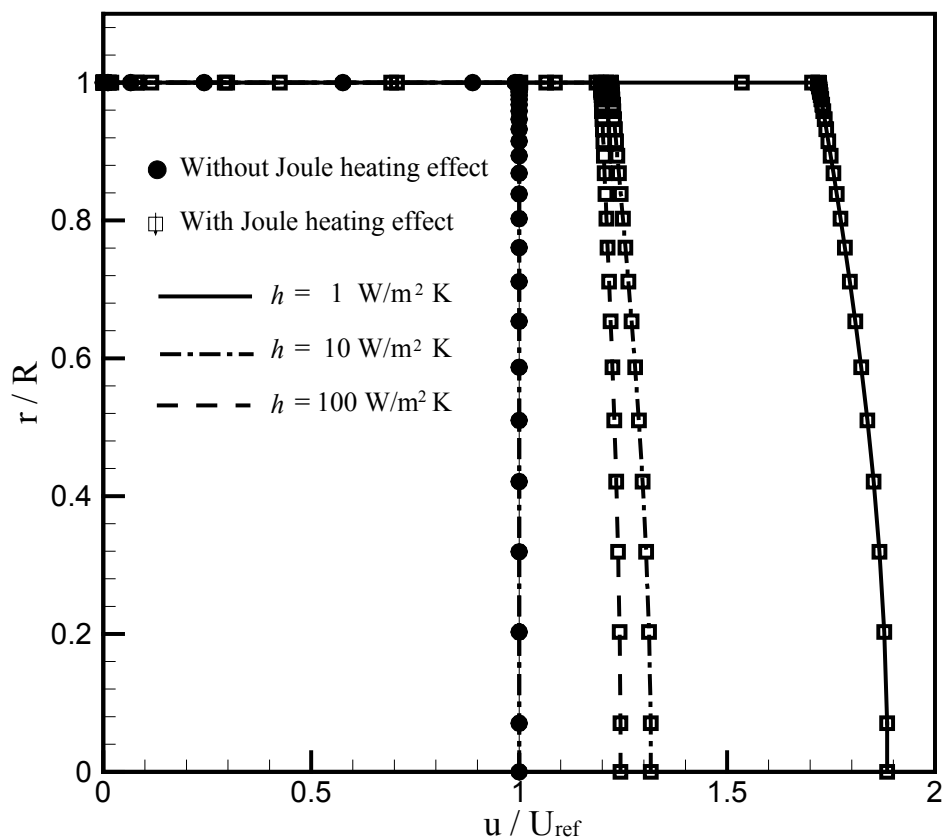


Fig. 5-17 Solution radial velocity distributions in a microcapillary under influences of the heat transfer coefficient outside the capillary wall. Other parameters used in computations are $R = 100 \mu m$, $C = 10^{-1} M$, $\zeta = -50 mV$, and $E_0 = 500 V/cm$.

5.6 Joule heating effect on the applied electrical field

Since the electrical conductivity of electrolyte solution is strongly dependent on the temperature, the presence of the Joule heating induced temperature field would cause a variation of the electrical conductivity of electrolyte. When Joule heating is considered, Joule heating induced temperature gradient will lead to a non-uniform electric field and hence the conservation of charges is assured. As the local electric conductivity increases proportionally with temperature elevation and higher local electric conductivity leads to lower local electric field strength. Therefore the electric field strength becomes higher at the entrance region where the temperature is under development, and becomes lower and constant in the thermally developed region. Fig.5-18 shows the variation of the electric field strength along the flow direction.

If the applied electric field strength is assumed to be constant, the viscosity and dielectric constant of the solution are the only parameters through which Joule heating affects the local electroosmotic flow. While considering the non-uniform electric field, other than the viscosity and dielectric constant, the electric field is another factor affecting the electroosmotic flow in the presence of the Joule heating. Hence such non-uniform applied electric field can result in a significantly different characteristic of the electroosmotic flow from that if a uniform electric applied field is assumed. Fig. 5-19 presents the steady-state axial velocity vectors in both the developing and the developed regions for (a) without Joule heating effect, (b) with Joule heating effect and (c) with Joule heating effect but assuming constant electric field strength. It is found that no matter whether the electric field is assumed to be uniform or non-uniform, under the Joule heating effect, increment of the solution

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temperature can result in the increment of the *EOF* velocity (i.e. the length of the vectors increase).

In addition, another interesting finding from Fig. 5-19 is the velocity profiles. If non-uniform electric field is considered, the velocity distribution exhibits a concave shape in the developing region, while with the flow advances it becomes flat, and eventually reaches convex pattern in the developed region. In contrast, if the electric field is assumed to be uniform, the velocity distribution presents a convex shape in the developing region, while with the flow advance it becomes flat, and eventually reaches concave pattern in the developed region. This is attributed to the different induced inner pressure gradient as shown in Fig. 5-20 and Fig. 5-21, which respectively give the induced inner pressure distribution along the axial direction of capillary for non-uniform (Fig.5-20) and uniform electric fields (Fig. 5-21). It can be found from Fig. 5-20 and Fig. 5-21 that in the developing region, a positive pressure gradient (pressure increases along the flow direction) is induced to decrease the liquid velocity under the non-uniform electric field, while a negative pressure gradient is induced to speedup the liquid velocity under the uniform electric field. On the contrary, in the developed region, a negative pressure gradient is induced to increase the liquid velocity under the non-uniform electric field, and a positive pressure gradient is induced to balance the liquid velocity under the uniform electric field, thus leading to different shapes of the *EOF* velocity profiles along the flow direction as shown in Fig. 5-19.

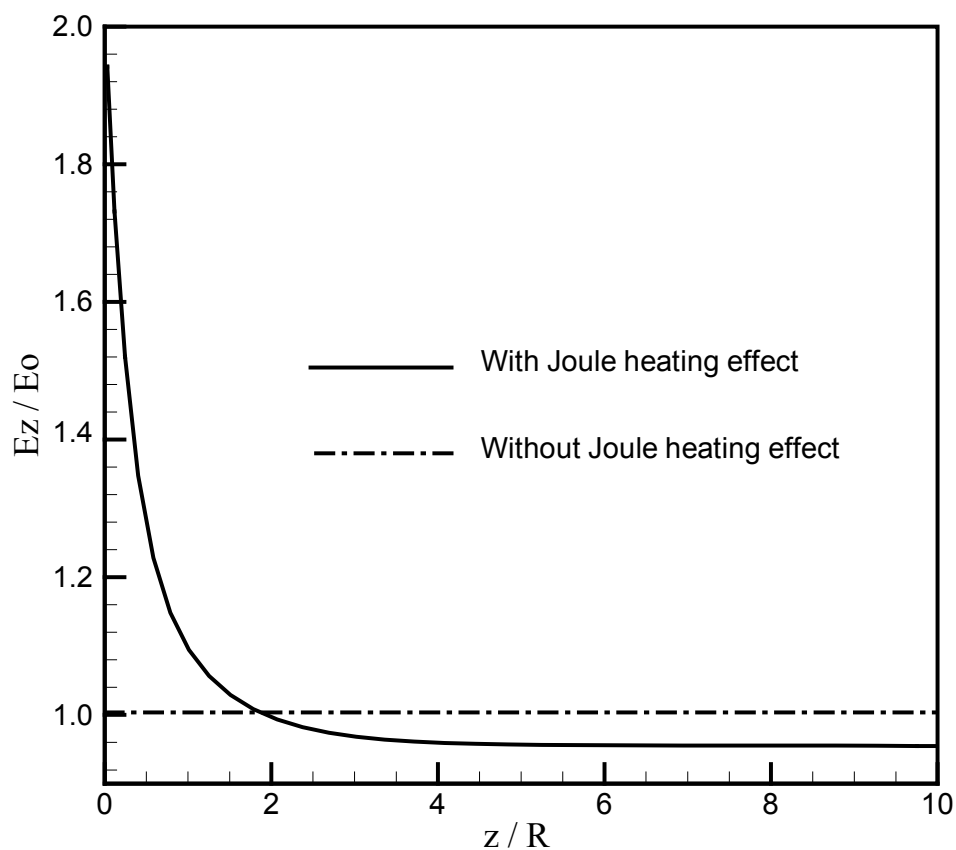


Fig. 5-18 Variation of the electric field strength along the axial direction. The parameters used in the computation are $R = 100 \mu m$, $E_0 = 500 V/cm$, $C = 10^{-1} M$, $\zeta = -50 mV$, and $h = 10 kW/m^2 K$.

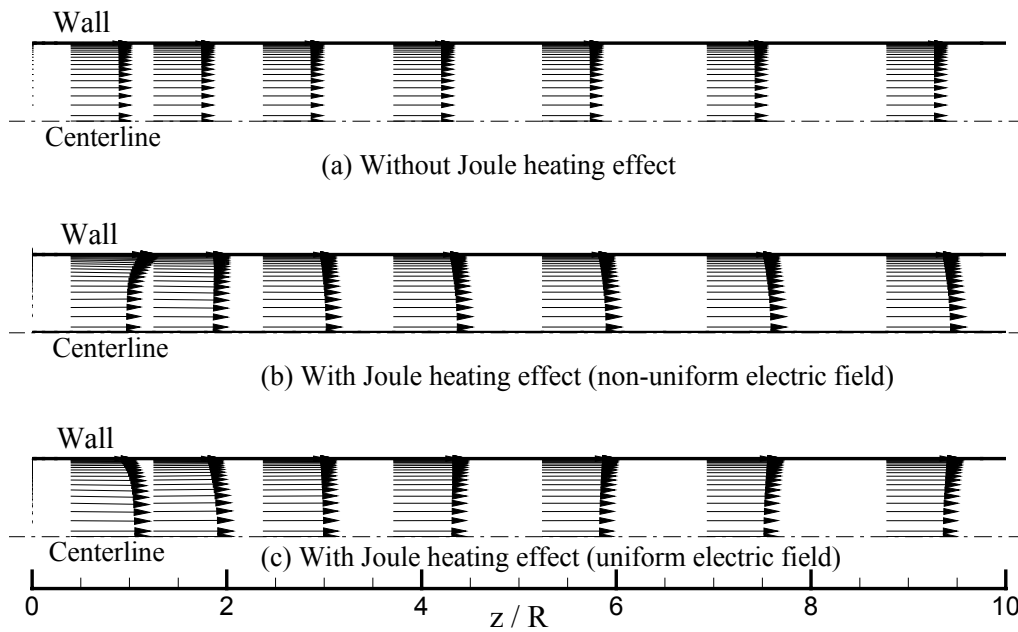


Fig. 5-19 The steady-state *EOF* velocity vectors in the both the developing and the fully developed regions for (a) without Joule heating effect, (b) with Joule heating effect and (c) with Joule heating effect (assume constant electric field strength). The parameters used in the computation are $R = 100 \mu m$, $E_0 = 500 V/cm$, $C = 10^{-1} M$, $\zeta = -50 mV$, and $h = 10 kW/m^2 K$

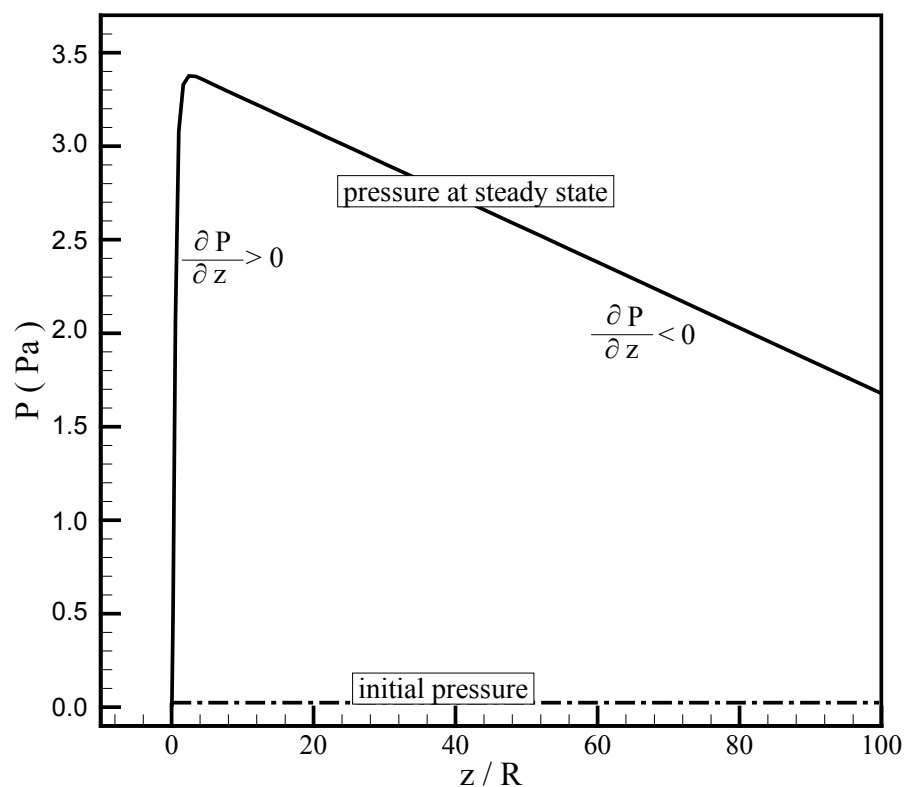


Fig. 5-20 Induced inner pressure distribution along the axial direction of capillary for non-uniform electric field. The parameters used in the computation are $R = 100\mu m$, $E_0 = 500V/cm$, $C = 10^{-1}M$, $\zeta = -50mV$, and $h = 10kW/m^2K$

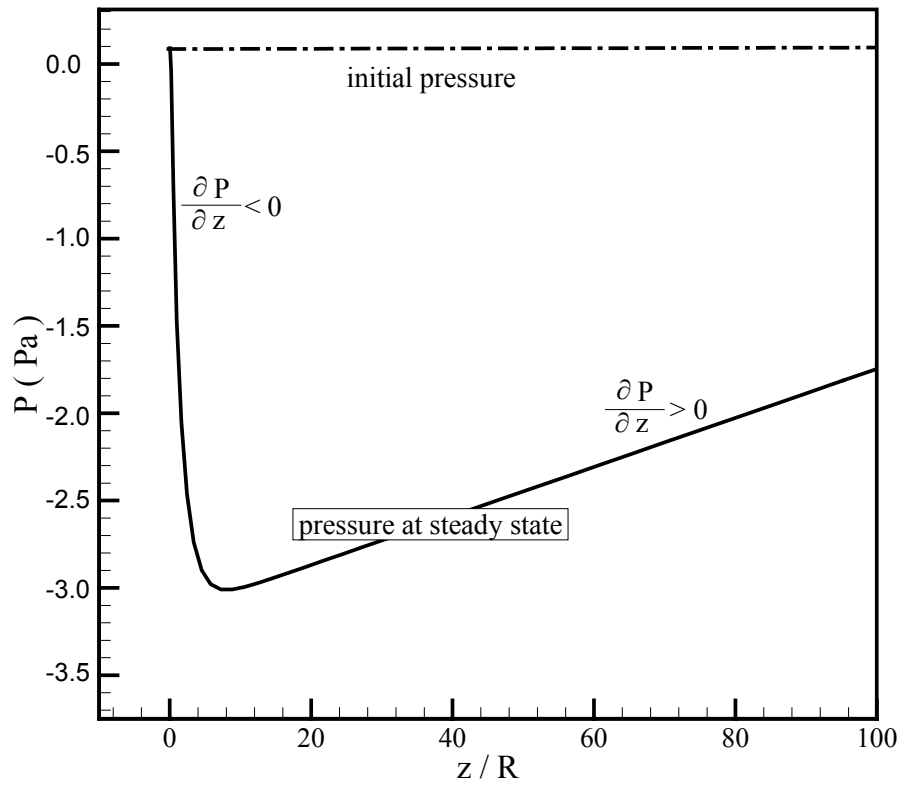


Fig. 5-21 Induced inner pressure distribution along the axial direction of capillary when the electric field is assumed as uniform. The parameters used in the computation are $R = 100\mu m$, $E_0 = 500V/cm$, $C = 10^{-1}M$, $\zeta = -50mV$, and $h = 10kW/m^2 K$

5.7 Joule heating effect on sample transport

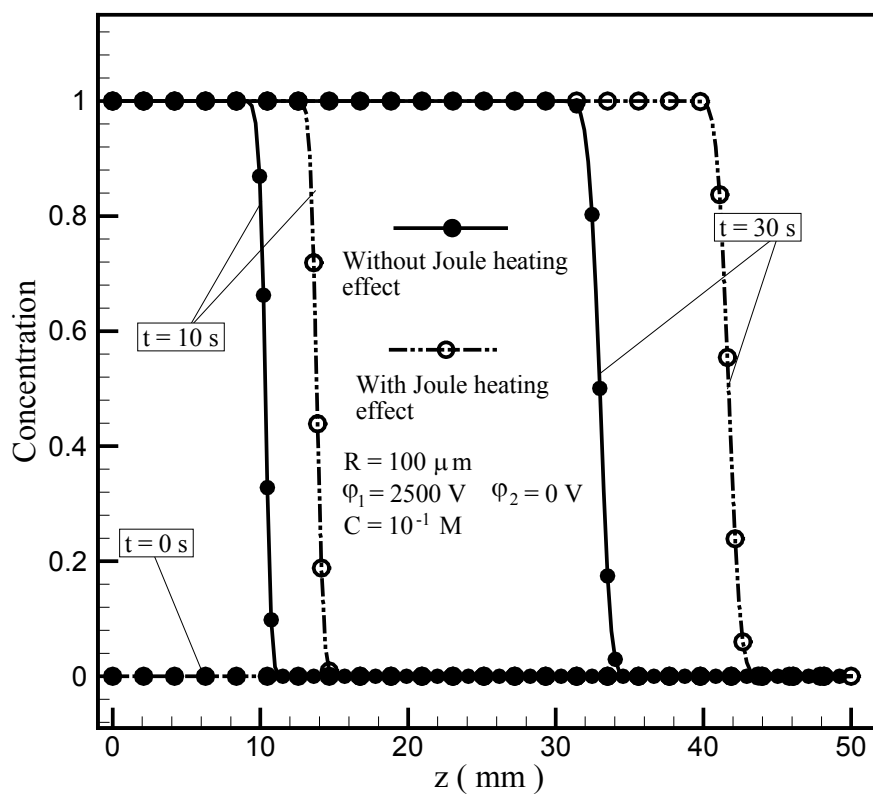
In this section, the DNA species is chosen as the sample transported in the microcapillary. According to *Ohara et al.* (2003), its mass diffusivity and electrophoretic mobility (at 25°C) are $D_{s0} = 2.01 \times 10^{-10} \text{ m}^2/\text{s}$ and $\mu_{ep0} = v_{ep0} = -2.74 \times 10^{-8} \text{ m}^2/\text{Vs}$, respectively.

For Case I, the translating interface, the computed sample concentration distributions are shown in Fig. 5-22 for (a) axial variation of the cross-sectional average of the sample concentration and (b) time evolution of the sample concentration distributions. Because of the low diffusion coefficient of sample species (for DNA, $D_i = 10^{-10} \text{ m}^2/\text{s}$, (*Ohara, et al.*, 2003)), the Schmidt number for the DNA sample species is much larger (of order 10^3). Typical Reynolds number in our case studies is of order 10^1 . Hence, we can estimate that the Peclet number $Pe = Re Sc$ is of order 10^2 , suggesting that the diffusion of the sample species is negligible as compared to the convection. The species transport is dominated by convection and mainly transported with the flow. Without Joule heating effects, it is noted that the sample concentration exhibits a flat interface as shown in Fig. 5-22(b). which is a unique advantage of electrokinetic transport mode adopted in the BioMEMS design. In the presence of the Joule heating, it can be seen from Fig. 5-22(a) & 5-22(b) that the sample transports much faster due to an increase of the EOF velocity. The detailed discussion of the Joule heating induced temperature field and its effects on the EOF was addressed in the previous section. In addition, as the sample electrophoresis mobility increases with increasing temperature, the Joule heating induced radial temperature variation gives rise to a change of the sample axial electrophoresis mobility along the radial direction, and hence, distorts the translating interface as

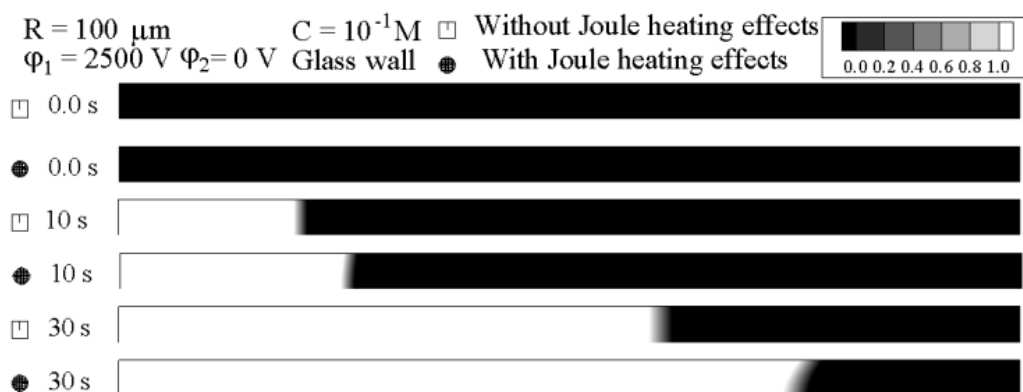
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shown in Fig. 5-22(b). Since the direction of the electrophoretic velocity for negatively charged samples (e.g., DNA species) is opposite to that of the *EOF* velocity, it can be clearly observed from Fig. 5-22(b) that the sample species in the central region is transported much slower than that close to the wall region, and such difference becomes larger as time elapses.

The numerical simulation of Case II, the dispersion of a finite sample plug, is presented in Fig. 5-23 for (a) axial variation of the cross-sectional average of the sample concentration and (b) time evolution of the sample concentration distributions. As can be seen in Fig. 5-23(b), in the absence of the Joule heating, the sample band exhibits a plug-like shape which is desirable for the detection in the capillary electrophoresis systems. With the Joule heating effects, for the same reasons discussed earlier, the samples not only transport faster, but also the sample peak decreases and the sample band deviates from its original plug-like shape as quantitatively shown in Fig. 5-23(a). This finding suggests that as the Joule heating is concerned, the dispersive effect on sample band shapes needs to be considered in the design and operation of capillary electrophoresis systems.

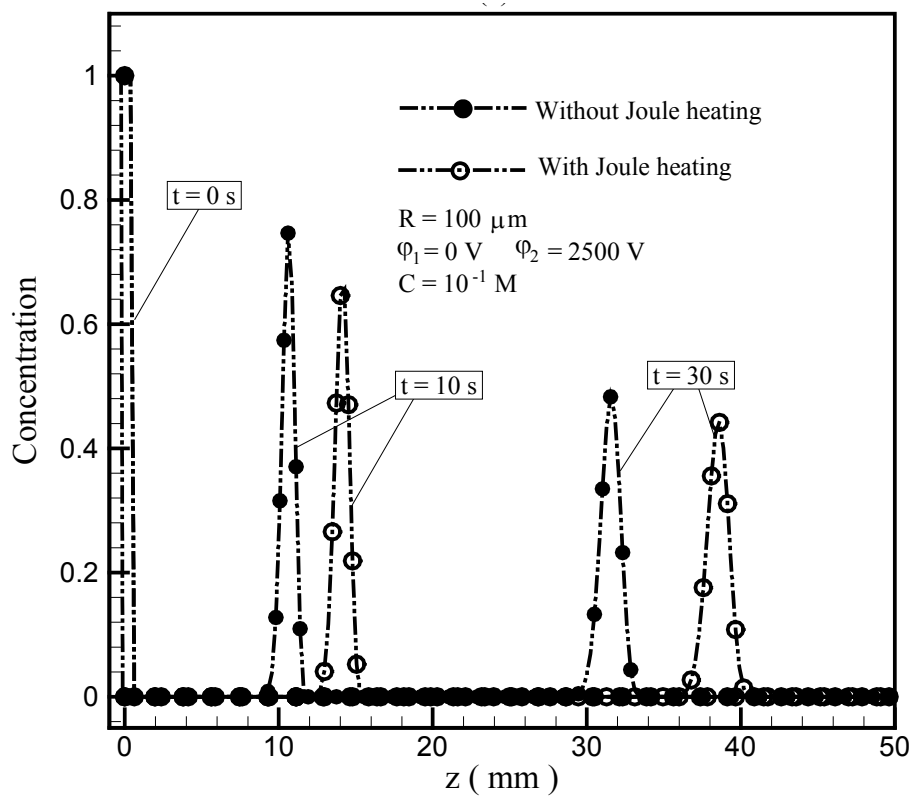


(a)

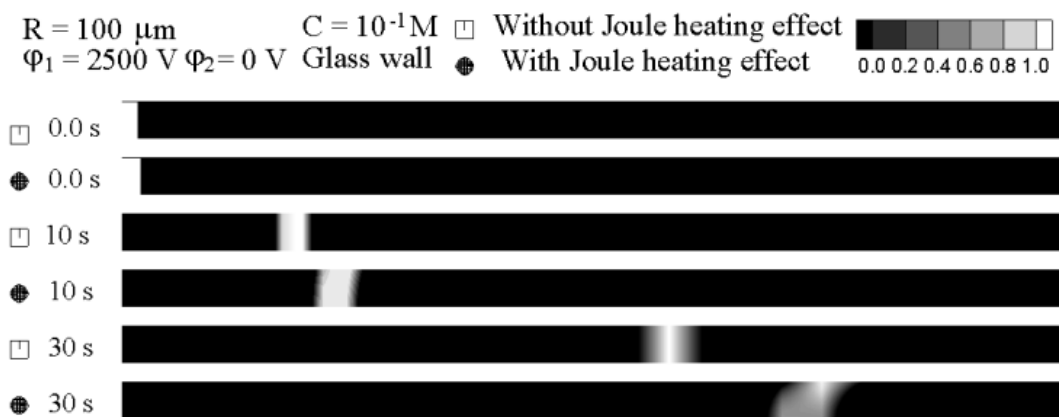


(b)

Fig. 5-22 Simulation results of the sample concentration distributions for Case I, the translating interface with/without Joule heating effects: (a) axial variation of the cross-sectional average of the sample concentration and (b) time evolution of the sample concentration distributions



(a)



(b)

Fig. 5-23 Simulation results of the sample concentration distributions for Case II, the dispersion of samples with/without Joule heating effects: (a) axial variation of the cross-sectional average of the sample concentration and (b) time evolution of the sample concentration distributions

5.8 Summary

Mathematical models for describing the transient Joule heating induced temperature field and its effects on the electroosmotic flow and electrokinetic transport of sample species in the commercial capillary electrophoresis system under the thermostated cooling mode are numerically solved by using the finite-volume based CFD technique. The simulations demonstrate that due to the coupling between the *EOF* field and the temperature field, the *EOF* has almost the same entrance length as the Joule heating induced temperature development. The Joule heating causes the development of both radial and axial temperature distributions in the capillary. It is found that the Joule heating effect is significant for large-sized capillaries, concentrated buffer solutions, high externally applied electric field strengths, and less effective cooling modes outside the capillary.

In addition, the simulations reveal that the presence of Joule heating could have a great impact on the electroosmotic flow and sample species transport. It not only causes the *EOF* to deviate from its normal flat profile, i.e. cause the *EOF* to exhibit a concave shape in the developing region and a parabolic pattern in the fully developed region, but also makes the sample species axially transport faster and be more dispersive along the radial direction of the capillary (i.e. deviate from its flat translating interface or plug-like sample band shape).

CHAPTER 6

JOULE HEATING AND ITS EFFECTS IN RECTANGULAR MICROCHANNELS

6.1 Introduction

It is well known that the microfluidics-based Lab-on-chip devices used for capillary electrophoresis and electrokinetic transport can be integrated together on a planar device using micro-fabrication technique. For practical microfluidic devices, the cross-section of microchannels made by modern micromachining technology is close to a rectangular shape (see Fig. 6-1). Moreover, the microchannels used in the experimental study in this thesis are of rectangular shape. Therefore, three-dimensional (3D) mathematical models describing Joule heating and its effects on the EOF and sample transport in a rectangular cross-section microchannel will be formulated in this chapter. The corresponding numerical scheme for solving the proposed 3D models will also be developed. Since the Joule number introduced in the model shows combined effects of several parameters including the buffer concentration, applied electric field strength and channel size, the parameters study in this chapter only involves the Joule number and the wall thickness. In addition, low cost polymeric materials such as poly(dimethylsiloxane) (PDMS), poly(methylmethacrylate) (PMMA) etc. are increasingly used in the fabrication of microfluidic systems because they offer an attractive alternative to traditional materials such as glass or silicon. Furthermore, use of polymeric materials tends to involve faster, simpler and significantly less expensive manufacturing techniques (for example: casting, injection and replica moulding, and hot embossing) than those used on the glass or silicon wafers. However, the low thermal conductivities inherent in

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polymeric materials (e.g. $0.18 \text{ W} / \text{m}^{-1} \text{K}^{-1}$ for PDMS which is an order of magnitude lower than that of glass) retards the rejection of internally generated Joule heat during the electrokinetic flow. Therefore, Joule heat and its effects in the rectangular microchannels fabricated by different materials will also be discussed in this chapter.

6.2 Governing equations

Consider an electrokinetic flow in microchannels of a rectangular cross-section as shown in Fig. 6-1.

Similar to Chapter 4 and Chapter 5, based on the Boltzmann assumption, the dimensionless mathematical models for the electroosmotic flow and mass species transport in a 3D Cartesian system can be written as:

6.2.1 Poisson – Boltzmann equation

$$\frac{\partial}{\partial x} \left[\frac{-\partial \bar{\psi}}{\varepsilon \partial x} \right] + \frac{\partial}{\partial y} \left[\frac{-\partial \bar{\psi}}{\varepsilon \partial y} \right] + \frac{\partial}{\partial z} \left[\frac{-\partial \bar{\psi}}{\varepsilon \partial z} \right] = (\kappa H)^2 \sinh(\bar{\psi}) \quad (6-1)$$

where H is the height of the micro-channel.

6.2.2 Laplace equation

$$\frac{\partial}{\partial x} \left[\frac{\bar{\lambda} \partial \bar{\phi}}{\partial x} \right] + \frac{\partial}{\partial y} \left[\frac{\bar{\lambda} \partial \bar{\phi}}{\partial y} \right] + \frac{\partial}{\partial z} \left[\frac{\bar{\lambda} \partial \bar{\phi}}{\partial z} \right] = 0 \quad (6-2)$$

6.2.3 Navier-Stokes equations

$$\frac{\partial \bar{u}}{\partial x} + \frac{\partial \bar{v}}{\partial y} + \frac{\partial \bar{w}}{\partial z} = 0 \quad (6-3)$$

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$$\begin{aligned}
& \bar{u} \frac{\partial \bar{u}}{\partial x} + \bar{v} \frac{\partial \bar{u}}{\partial y} + \bar{w} \frac{\partial \bar{u}}{\partial z} \\
& = -\frac{\partial \bar{p}}{\partial x} + \frac{1}{\text{Re}} \left\{ \frac{\partial}{\partial x} \left[\bar{\mu} \frac{\partial \bar{u}}{\partial x} \right] + \frac{\partial}{\partial y} \left[\bar{\mu} \frac{\partial \bar{u}}{\partial y} \right] + \frac{\partial}{\partial z} \left[\bar{\mu} \frac{\partial \bar{u}}{\partial z} \right] \right\} - B_3 \bar{E}_x \sinh(\bar{\psi})
\end{aligned} \tag{6-4a}$$

$$\begin{aligned}
& \bar{u} \frac{\partial \bar{v}}{\partial x} + \bar{v} \frac{\partial \bar{v}}{\partial y} + \bar{w} \frac{\partial \bar{v}}{\partial z} \\
& = -\frac{\partial \bar{p}}{\partial y} + \frac{1}{\text{Re}} \left\{ \frac{\partial}{\partial x} \left[\bar{\mu} \frac{\partial \bar{v}}{\partial x} \right] + \frac{\partial}{\partial y} \left[\bar{\mu} \frac{\partial \bar{v}}{\partial y} \right] + \frac{\partial}{\partial z} \left[\bar{\mu} \frac{\partial \bar{v}}{\partial z} \right] \right\} - B_3 \bar{E}_y \sinh(\bar{\psi})
\end{aligned} \tag{6-4b}$$

$$\begin{aligned}
& \bar{u} \frac{\partial \bar{w}}{\partial x} + \bar{v} \frac{\partial \bar{w}}{\partial y} + \bar{w} \frac{\partial \bar{w}}{\partial z} \\
& = -\frac{\partial \bar{p}}{\partial z} + \frac{1}{\text{Re}} \left\{ \frac{\partial}{\partial x} \left[\bar{\mu} \frac{\partial \bar{w}}{\partial x} \right] + \frac{\partial}{\partial y} \left[\bar{\mu} \frac{\partial \bar{w}}{\partial y} \right] + \frac{\partial}{\partial z} \left[\bar{\mu} \frac{\partial \bar{w}}{\partial z} \right] \right\} - B_3 \bar{E}_z \sinh(\bar{\psi})
\end{aligned} \tag{6-4c}$$

$$\bar{E}_x = -\frac{\phi_0}{HE_0} \frac{\partial \bar{\phi}}{\partial x} \quad \bar{E}_y = -\frac{\phi_0}{HE_0} \frac{\partial \bar{\phi}}{\partial y} \quad \bar{E}_z = -\frac{\phi_0}{HE_0} \frac{\partial \bar{\phi}}{\partial z} \tag{6-4d}$$

$$B_3 = \frac{H\sigma n_0 E_0}{\rho U_{\text{ref}}^2 / 2} \tag{6-4e}$$

where $\bar{u}, \bar{v}, \bar{w}$ are the components of the dimensionless electroosmotic velocity in x, y, z direction, respectively

6.2.4 Energy equation

$$\begin{aligned}
& \bar{u} \frac{\partial \bar{T}}{\partial x} + \bar{v} \frac{\partial \bar{T}}{\partial y} + \bar{w} \frac{\partial \bar{T}}{\partial z} = \\
& \frac{1}{\text{RePr}} \left\{ \frac{\partial}{\partial x} \left[\bar{k}_l \frac{\partial \bar{T}}{\partial x} \right] + \frac{\partial}{\partial y} \left[\bar{k}_l \frac{\partial \bar{T}}{\partial y} \right] + \frac{\partial}{\partial z} \left[\bar{k}_l \frac{\partial \bar{T}}{\partial z} \right] \right\} + \frac{Jo}{\text{RePr}} \bar{q}
\end{aligned} \tag{6-5a}$$

$$\bar{E} = \sqrt{\bar{E}_x^2 + \bar{E}_y^2 + \bar{E}_z^2} \quad \bar{q} = \bar{\lambda} \bar{E}^2 \tag{6-5b}$$

In addition, the conjugated heat transfer in the channel wall is governed by

$$\frac{\partial}{\partial \bar{x}} \left[\bar{k} \frac{\partial \bar{T}}{\partial \bar{x}} \right] + \frac{\partial}{\partial \bar{y}} \left[\bar{k} \frac{\partial \bar{T}}{\partial \bar{y}} \right] + \frac{\partial}{\partial \bar{z}} \left[\bar{k} \frac{\partial \bar{T}}{\partial \bar{z}} \right] = 0 \quad (6-6)$$

6.2.5 Mass transport equation

$$\begin{aligned} \frac{\partial \bar{C}_s}{\partial \bar{t}} + \text{Re} \left[(\bar{u} + \bar{u}_{ep}) \frac{\partial \bar{C}_s}{\partial \bar{x}} + (\bar{v} + \bar{v}_{ep}) \frac{\partial \bar{C}_s}{\partial \bar{y}} + (\bar{w} + \bar{w}_{ep}) \frac{\partial \bar{C}_s}{\partial \bar{z}} \right] \\ = \frac{1}{Sc} \left\{ \frac{\partial}{\partial \bar{x}} \left[\bar{D}_s \frac{\partial \bar{C}_s}{\partial \bar{x}} \right] + \frac{\partial}{\partial \bar{y}} \left[\bar{D}_s \frac{\partial \bar{C}_s}{\partial \bar{y}} \right] + \frac{\partial}{\partial \bar{z}} \left[\bar{D}_s \frac{\partial \bar{C}_s}{\partial \bar{z}} \right] \right\} \end{aligned} \quad (6-7)$$

where, $\bar{u}_{ep}$, $\bar{v}_{ep}$, and $\bar{w}_{ep}$ are the components of the dimensionless electrophoretic velocity in x, y, z direction, respectively.

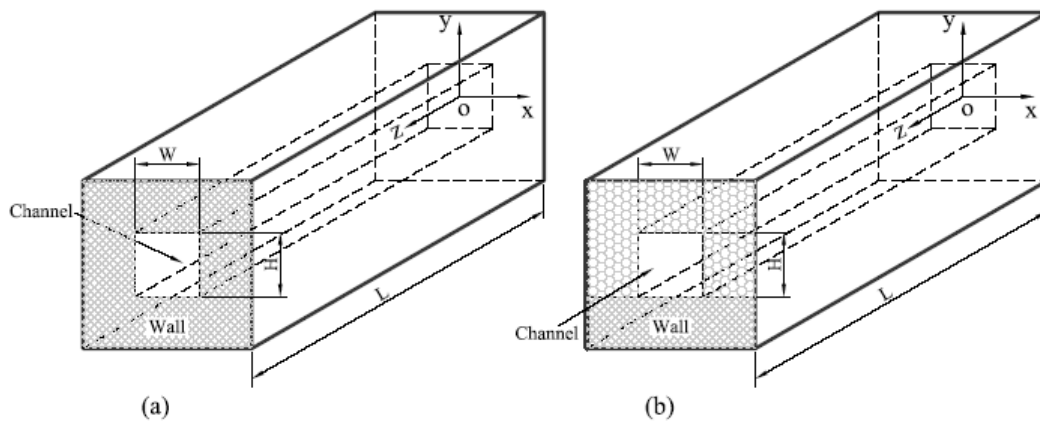


Fig. 6-1 Schematic diagram of a rectangular cross-sectional microchannel: (a) commercial silica glass channel; (b) fabricated PDMS-PDMS or Glass-PDMS channel.

6.3 Joule heating and its effects in straight channels

6.3.1 Initial and boundary conditions

A straight microchannel is selected because it is the most general segment in a microfluidic system. For such a straight channel (Fig. 6-1), due to its symmetry, a

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quarter or a half of the channel cross-section is chosen in the computation, and it is shown in Fig 6-2. Hence the boundary conditions for above listed governing equations describing the steady-state Joule heating and its effects on the electroosmotic flow can be written as:

At the Inlet, $\bar{z} = 0$

$$\bar{T} = 1.0 \quad \bar{\psi} = 0 \quad \bar{\phi} = 1.0 \quad \bar{u} = 0 \quad \bar{v} = 0 \quad \frac{\partial \bar{w}}{\partial \bar{z}} = 0 \quad (6-8a)$$

At the outlet, $\bar{z} = L/H$

$$\frac{\partial \bar{T}^2}{\partial \bar{z}^2} = 0 \quad \frac{\partial \bar{\psi}}{\partial \bar{z}} = 0 \quad \bar{\phi} = 0.0 \quad \frac{\partial \bar{u}}{\partial \bar{z}} = 0 \quad \frac{\partial \bar{v}}{\partial \bar{z}} = 0 \quad \frac{\partial \bar{w}}{\partial \bar{z}} = 0 \quad (6-8b)$$

At the symmetric planes, $\bar{x} = 0$ and $\bar{y} = 0$ for the commercial silica glass channels or $\bar{x} = 0$ for the fabricated channels

$$\frac{\partial \bar{T}}{\partial \bar{x}} = 0 \quad \frac{\partial \bar{\psi}}{\partial \bar{x}} = 0 \quad \frac{\partial \bar{\phi}}{\partial \bar{x}} = 0 \quad \bar{u} = 0 \quad \frac{\partial \bar{v}}{\partial \bar{x}} = 0 \quad \frac{\partial \bar{w}}{\partial \bar{x}} = 0 \quad (6-8c)$$

$$\frac{\partial \bar{T}}{\partial \bar{y}} = 0 \quad \frac{\partial \bar{\psi}}{\partial \bar{y}} = 0 \quad \frac{\partial \bar{\phi}}{\partial \bar{y}} = 0 \quad \frac{\partial \bar{u}}{\partial \bar{y}} = 0 \quad \bar{v} = 0 \quad \frac{\partial \bar{w}}{\partial \bar{y}} = 0 \quad (6-8d)$$

At the channel wall, $\bar{x} = W/H$ and $\bar{y} = 0.5$ for the commercial channels or $\bar{x} = W/H$ and $\bar{y} = \pm 0.5$ for the fabricated channels

$$\bar{\psi} = \bar{\zeta} \quad \frac{\partial \bar{\phi}}{\partial \bar{x}} = 0 \quad \bar{u} = 0 \quad \bar{v} = 0 \quad \bar{w} = 0 \quad (6-8e)$$

$$\bar{\psi} = \bar{\zeta} \quad \frac{\partial \bar{\phi}}{\partial \bar{y}} = 0 \quad \bar{u} = 0 \quad \bar{v} = 0 \quad \bar{w} = 0 \quad (6-8f)$$

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As the energy equation is solved together with the conjugated heat conduction equation, the temperature boundary conditions at outside surface of the microchannel are

$$-\bar{k}_s \left. \frac{\partial \bar{T}}{\partial x} \right|_{\text{outersurface}} = \frac{hH}{k_{ref}} (\bar{T} - 1) \quad (6-9a)$$

$$-\bar{k}_s \left. \frac{\partial \bar{T}}{\partial y} \right|_{\text{outersurface}} = \frac{hH}{k_{ref}} (\bar{T} - 1) \quad (6-9b)$$

In this section, the Joule heating effects on the dispersion of a finite sample plug in a rectangular microchannel will be studied, that is the Case II mentioned in chapter 5. For the transient sample transport, the initial and boundary conditions can be expressed as:

The initial condition ($\bar{t} = 0$):

$$\begin{cases} \bar{C}_s = 1.0 & (z/H \leq l_0) \\ \bar{C}_s = 0.0 & (z/H > l_0) \end{cases} \quad (6-10a)$$

In the computation, l_0 was chosen as $l_0 = 5H$.

The boundary conditions are

$$\text{Inlet:} \quad \bar{C}_s = 0.0 \quad (6-10b)$$

$$\text{Outlet:} \quad \frac{\partial^2 \bar{C}_s}{\partial z^2} = 0 \quad (6-10c)$$

$$\text{Symmetry planes:} \quad \frac{\partial \bar{C}_s}{\partial x} = 0 \quad \frac{\partial \bar{C}_s}{\partial y} = 0 \quad (6-10d)$$

$$\text{Channel wall:} \quad \frac{\partial \bar{C}_s}{\partial x} = 0 \quad \frac{\partial \bar{C}_s}{\partial y} = 0 \quad (6-10e)$$

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As the Joule number has combined the effects of several parameters including the buffer concentration (λ_0), applied electric field (E_0), channel geometry (H) on the temperature distributions, further on the electroosmotic flow and sample transport, which it does not includes the effects of the wall thickness and wall material. Hence in this chapter, parametric study includes the Joule number, microchannel wall thickness and wall material. Further, different from the commercial capillary electrophoresis systems discussed in Chapter 5, for fabricated microfluidic systems, the special thermostated cooling mode is generally not included, and the Joule heat is mainly dissipated from the microchannel surface by mean of air natural convection. Thus the heat transfer coefficient outside the microchannel is chosen as $h = 10W / m^2 K$. In addition, the microchannels in the calculations have a length of $L = 20\text{ mm}$ and cross-section of $100\mu m \times 100\mu m$, and with different wall thickness and wall materials. The working fluid is $NaHCO_3$ solution and its properties are taken to be the same as water: density $\rho = 998kg / m^3$, specific heat capacity $4180kJ / (kgK)$, and thermal conductivity $k_l = 0.6W / (mK)$ (at room temperature $298K$). The electric conductivity for $NaHCO_3$ solution (at room temperature $20^\circ C$) $\lambda_{+0} = 50.08 \times 10^{-4} m^2 S / mol$ (Na^+) and $\lambda_{-0} = 44.5 \times 10^{-4} m^2 S / mol$ (HCO_3^-) (Weast, et al., 1986).

6.3.2 Temperature distributions and velocity field

6.3.2.1 Effect of the Joule number

In the model development, the Joule number is introduced and it characterizes the magnitude of the Joule heating.

Variation of the liquid solution temperature at the channel centerline along the flow direction for different Joule numbers is shown in Fig 6-3. In the calculation, the

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Joule number is chosen as 0.057, 0.089 and 0.128, corresponding to the situations where a $100\mu\text{m} \times 100\mu\text{m}$ silica microchannel filled with a $10^{-2} M \text{ NaHCO}_3$ electrolyte of the thermal conductivity as $k_l = 0.6 W / m \cdot K$ under applied electric fields ranged from 600 V/cm, 750 V/cm, to 900 V/cm.

Similar to the temperature profiles in a cylindrical capillary in the commercial electrophoresis system reported in Chapter 5, it is found from Fig.6-3 that the solution temperature starts at the room temperature at the entrance, and achieves fully developed temperatures downstream. However, the length of the thermal entrance region (or the thermal developing length) for the conditions used in the calculation is around $z / H \approx 50$, much larger than that reported in chapter 5 ($z / R \approx 3 \sim 5$) for the cylindrical capillary under thermostated liquid bath cooling mode. This is because the heat transfer coefficient used here for the natural convection cooling mode is $h = 10 W / m^2 K$, significantly lower than that used for the thermostated liquid bath cooling mode ($h = 10 kW / m^2 K$).

By comparing the temperature profiles shown in Fig. 6-3 with those shown in Chapter 5 (Fig. 5-10b), we can find that although the ratio of heat dissipation (measured by surface) to heat generation (defined by volume) is the same for the same hydraulic diameter, due to the special cooling mode used, it shows a commercial electrophoresis system can sustain much higher Joule numbers (thus stronger Joule heating) than a fabricated microfluidic system. For example, for the case where $R = 100\mu\text{m}$ shown in Fig 5-10b, the Joule number is 1.2 and the average solution temperature in the thermally developed region is lower than 320 K. While for the case of Joule number is 0.128 shown in Fig 6-3, the average solution temperature in the thermally developed region is higher than 325 K. In addition, it is seen from fig 6-3

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that as Joule number varies from 0.057 to 0.128, the temperature of the electrolyte increases substantially. This scenario can be explained using the definition of the Joule number, $J_0 = \frac{H^2 \lambda_0 E_0^2}{k_{ref} (T_0 - T_{ref})}$, a larger Joule number indicates a higher applied electric field strength, or larger size channel, or higher concentration of electrolyte (i.e. higher electric conductivity), or lower thermal conductivity of electrolyte. Nevertheless, Fig. 6-3 shows a higher Joule number combining all the parameters which leads to more heat generated and less heat dissipated and thus induces higher solution temperatures.

The steady temperature distributions in the solution and the solid wall along transverse x and y directions for different Joule numbers are respectively presented in Fig. 6-4, Fig. 6-5 and Fig. 6-6 in (a) the thermally developing region and (b) the thermally developed region.

It is demonstrated that the temperature variation along the x, y directions inside the solution and the channel wall is insignificant as compared to the temperature increase in both the thermally developing and developed region shown in Fig. 6-4, 6-5, 6-6. The phenomenon is due to the low Biot number of the system (as a rough estimation, $Bi = O(10^{-3})$). Because the Reynolds number of the electroosmotic flow is very small (i.e. $Re = O(10^{-1})$), the heat generated in the channel is dissipated mainly by thermal conduction through the channel wall and then by convection with the surrounding air, rather than by advection with the fluid flow. When $Bi \ll 1$, the resistance to heat conduction within the microfluidic system is much less than the resistance to thermal convection between the channel-wall surface and the surrounding air. Virtually, the temperature variation lies only between the outer wall and the surrounding air, whereas the temperature within the whole capillary system

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remains nearly uniform. This observation is different from that reported in Chapter 5, where the axial temperature difference between the capillary central line and the outside surface of the capillary is comparable to the temperature increment in the channel. This is because the Biot number of the special thermostated cooling system is about unity due to large heat transfer coefficient outside the wall. Thus, the resistance to heat conduction within the capillary system is comparable to the resistance to thermal convection across the channel wall-surrounding air boundary layer. However, with a close examination of the steady temperature distribution in $x-y$ direction shown in Figure 6-4, 6-5 and 6-6, we can find that the highest temperature still occurs at the channel centerline and decreases gradually along the $x-y$ direction. The temperature distribution in the channel shows a parabolic profile as shown in Fig. 6-7, which presents the temperature distribution in the thermally developed region.

Fig 6-8 compares the dimensionless electroosmotic flow vectors in both the developing and the fully-developed region for (a) without Joule heating effects and various Joule numbers including (b) $Jo = 0.057$, (c) $Jo = 0.089$ and (d) $Jo = 0.128$. As mentioned earlier, the electroosmotic flow velocity tends to increase with temperature primarily due to its inverse relationship with viscosity. As such it can be seen from Fig. 6-8 that the velocity vector for large Joule numbers (e.g. $Jo = 0.128$) is significantly larger than that for small Joule numbers (e.g. $Jo = 0.057$) due to higher temperature rise for large Joule numbers. Furthermore, similar to that discussed in chapter 5, the lower temperature near the inlet region leads to higher viscosity, and tends to induce smaller velocity. On the other hand, the lower temperature induced lower electric conductivity tends to increase the electric potential field gradient (i.e. local electric field strength) and tends to induce a larger velocity. However, according to the calculation, it can be found that the electric field increment is larger than the

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viscosity increment and hence leads to a larger velocity near the inlet region. In the contrary, in the thermally developed region, the higher temperature tends to result in a lower velocity than that in the entry region. In the microchannel, the conservation of the flow rate along the flow direction should be maintained and hence an inner pressure gradient is induced. Such inner pressure gradient will cause the electroosmotic flow velocity to exhibit quite different shape in the developing and fully-developed region as shown in Fig. 6-8, and such difference tends to increase with the increase of the Joule number. In addition, compared with that in the commercial capillary electrophoresis system with special thermostated cooling mode, a longer temperature developing region in such fabricated microfluidic system also leads to a longer velocity developing region. This can be demonstrated by comparing the results shown in Fig. 6-8 with the results shown in Fig. 5-19 in Chapter 5.

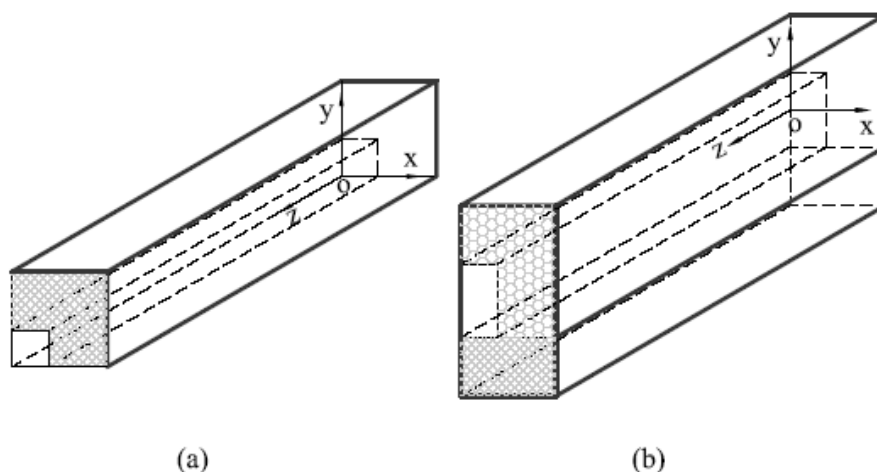


Fig. 6-2 Computation domain for a straight channel: (a) a quarter of the commercial silica glass channel; (b) a half of the fabricated PDMS/PDMS or Glass/PDMS channel.

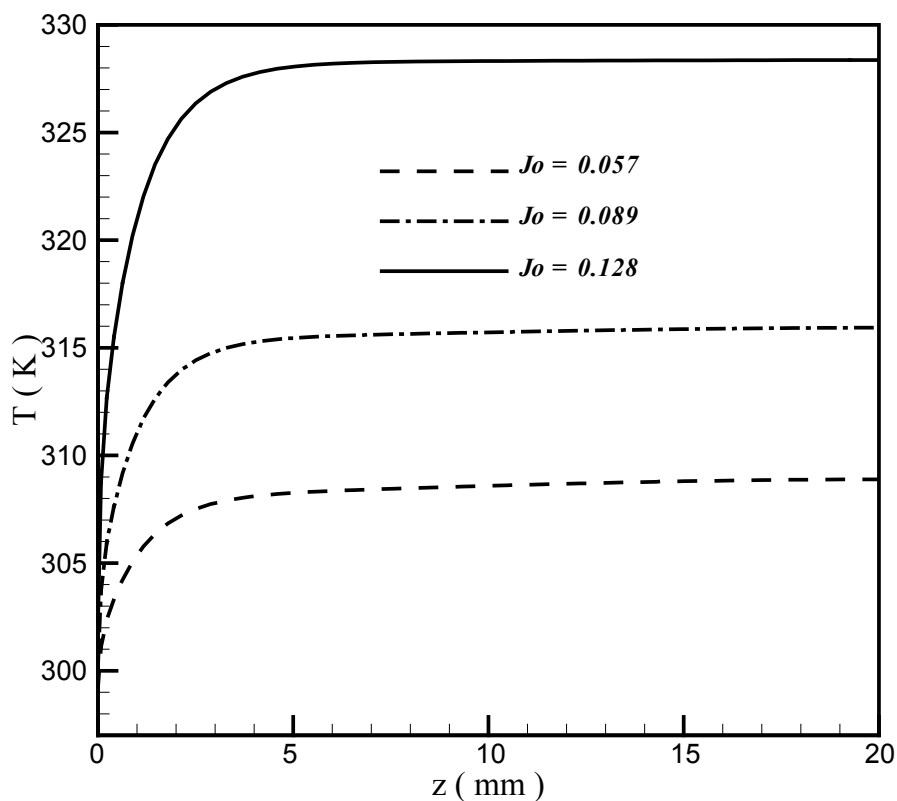
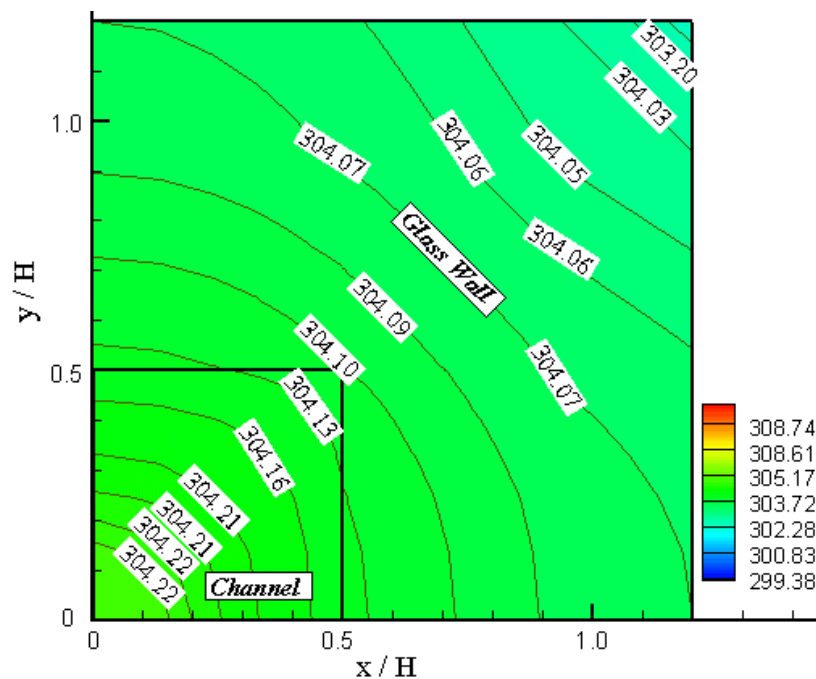
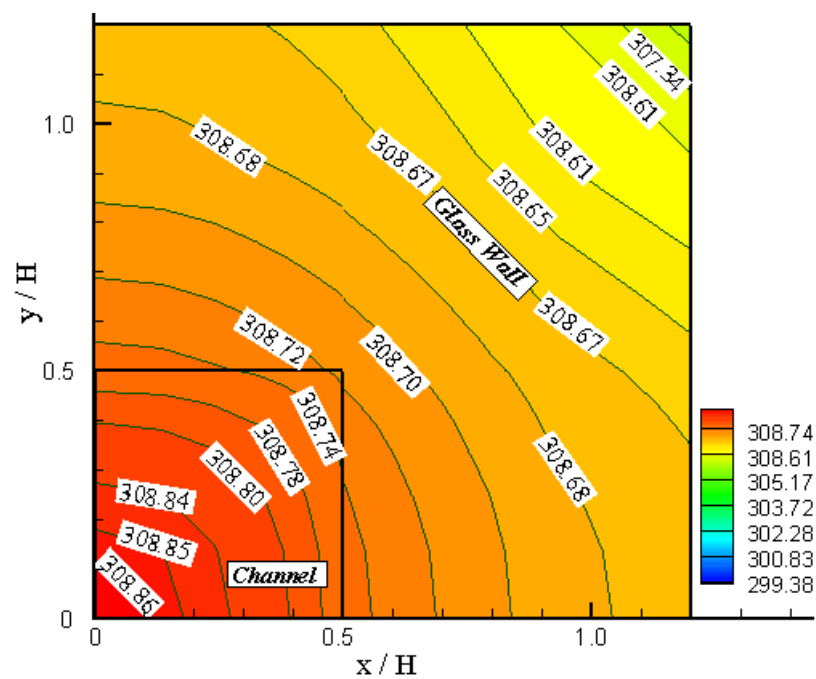


Fig. 6-3 Variation of the liquid temperature at the centerline of the commercial silica glass channel along the flow direction with different Joule numbers. The Joule numbers are corresponding to the following parameters: $C = 10^{-2} M$, $k_l = 0.6 W / m \cdot K$, $E_0 = 600 V/m$ ($Jo = 0.057$), $E_0 = 750 V/m$ ($Jo = 0.089$), and $E_0 = 900 V/m$ ($Jo = 0.128$) for a $100 \mu m \times 100 \mu m$ channel

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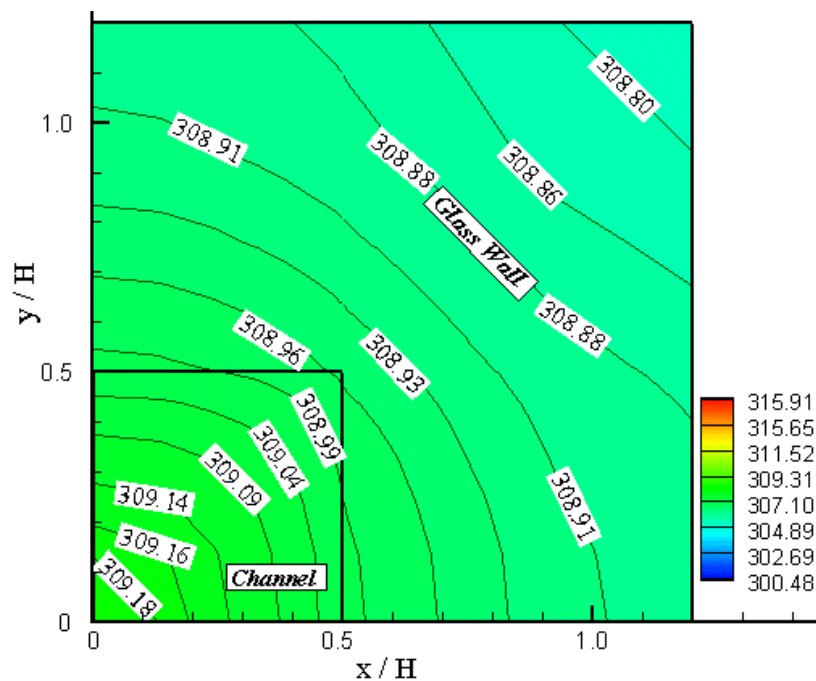


(a)

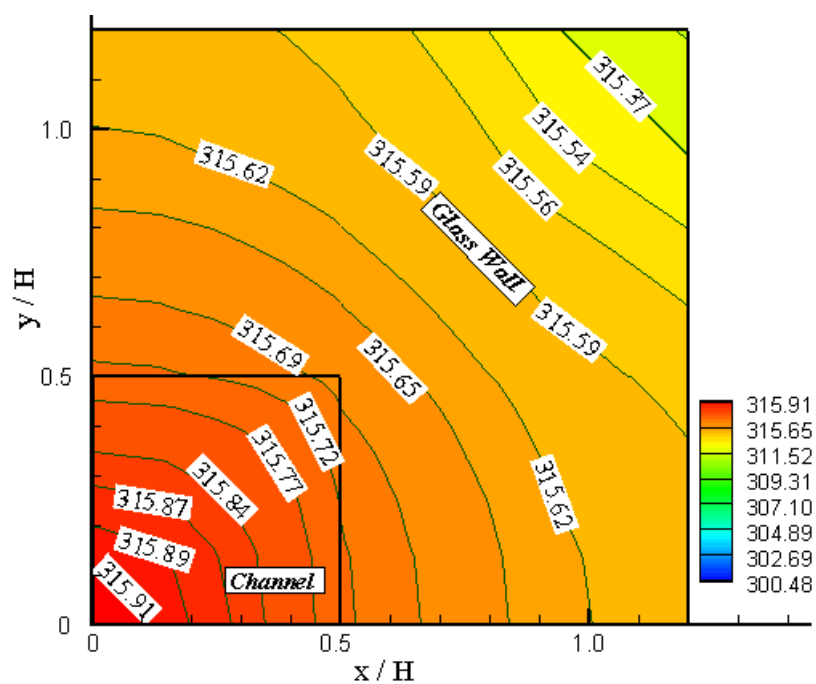


(b)

Fig. 6-4 Transverse cross-sectional temperature contour in both the channel (solution) and the solid wall for $Jo = 0.057$: (a) the thermally developing region ($z/H = 10$); (b) thermally developed region ($z/H = 178$).

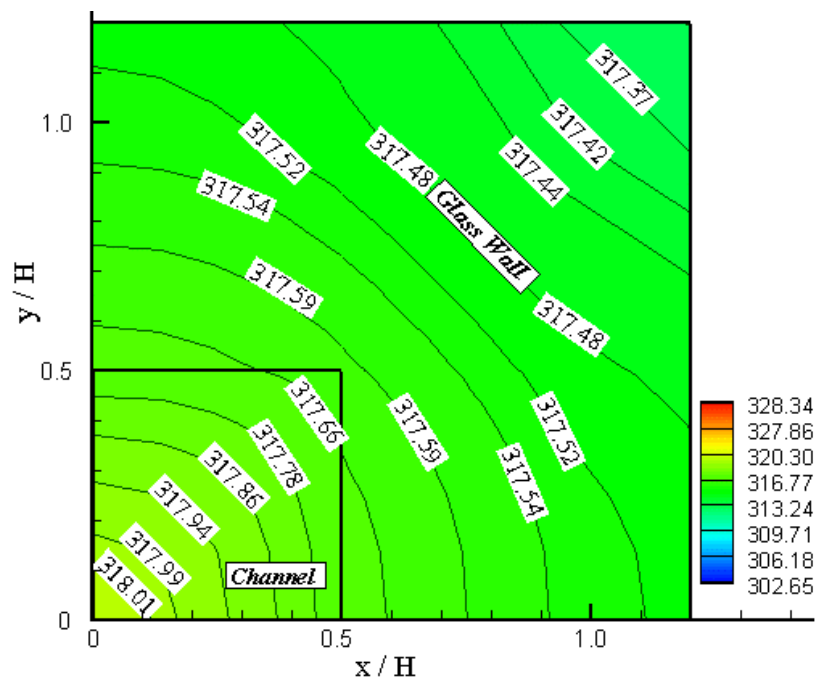


(a)

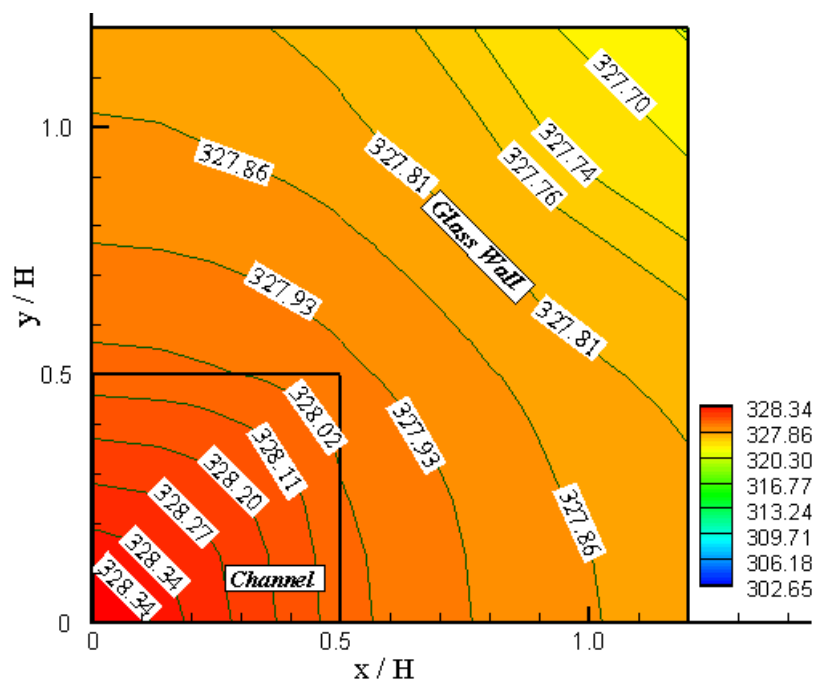


(b)

Fig. 6-5 Transverse cross-sectional temperature contour in both the channel (solution) and the solid wall for $Jo = 0.089$: (a) the thermally developing region ($z/H = 10$); (b) the thermally developed region.



(a)



(b)

Fig. 6-6 Transverse cross-sectional temperature contour in both the channel (solution) and the solid wall for $Jo = 0.128$: (a) the thermally developing region ($z/H = 10$); (b) the thermally developed region.

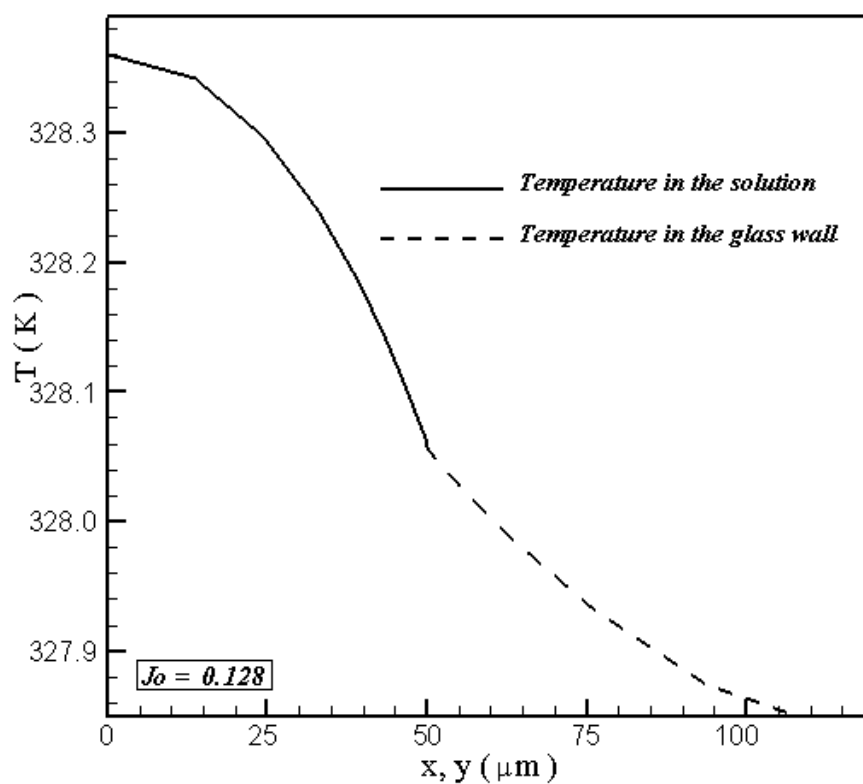


Fig. 6-7 Transverse temperature distribution in both the channel (solution) and glass wall along the x, y direction in the thermally developed region for a Joule number of 0.128

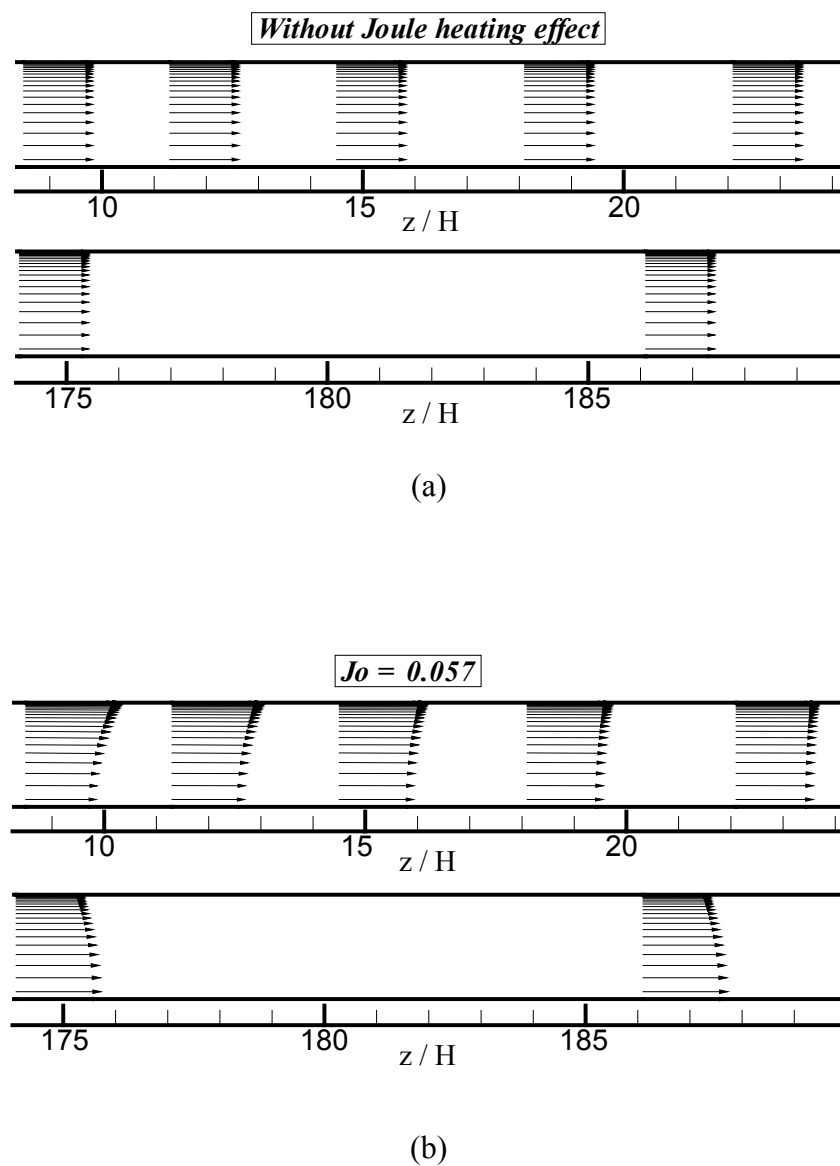


Fig. 6-8 The electroosmotic flow velocity vectors in both the developing and the fully developed regions for various Joule numbers: (a) without Joule heating effects; (b) $Jo = 0.057$.

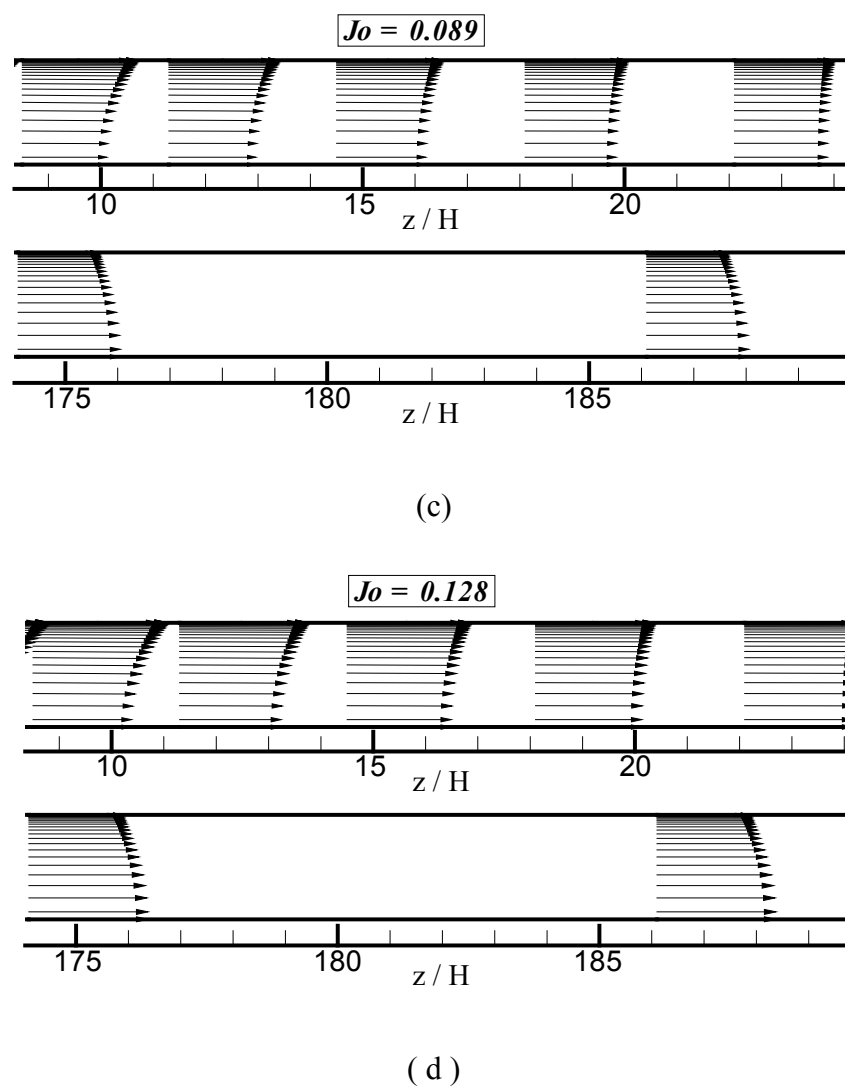


Fig. 6-8 The electroosmotic flow velocity vectors in both the developing and the fully developed regions for various Joule numbers: (c) $Jo = 0.089$; (d) $Jo = 0.128$

6.3.2.2 Effect of channel wall thickness

It will be interesting to examine how significantly the system temperature induced by the Joule heating will be affected by the wall thickness. For analysis, the channels made by Polymicro Technologies (Phonix, USA) were chosen. These channels have the same inner dimension but various outer dimensions. This means the thickness of channel wall varies accordingly.

The variation of the liquid temperature at the channel centerline along the flow direction for different wall thickness when the Joule number is 0.128 is shown in Fig 6-9. It is found from Fig. 6-9 that the temperatures of liquid solution in a channel with thin wall ($\Delta = 70\mu m$) are significantly higher than those in a channel with thick wall ($\Delta = 200\mu m$). The same trend can also be observed in the plots of the temperature distributions in x, y direction in both the liquid solution and solid wall shown in Fig. 6-10, 6-11, 6-12 for (a) the thermally developing region and (b) the thermally developed region. The scenario can be attributed to the fact that as the wall thickness increases, the ratio of the surface area to the volume increases, leading to a higher ratio of the heat dissipation (measured by surface) to the Joule heat generation (defined by volume), and hence resulting in lower temperature of the system.

Furthermore, it can also be found from Fig. 6-10, 6-11 and fig 6-12 that although the system temperature decreases with increase of the wall thickness, the temperature differences between the centerline and the outside surface of channel increases somewhat in both the thermally developing and the thermally developed region. This can be explained in the following. Since the resistance to heat conduction within the channel increases with the increase of the wall thickness, the temperature difference between the centerline and the outside surface increases as increasing the wall thickness. However, as discussed in the previous section, this resistance (i.e. to

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heat conduction within the channel) is much less than the resistance to thermal convection across the channel surface to surrounding air. As a result, the major temperature variation occurs between the outer wall and the surrounding. Therefore, the temperature difference between the centerline and the outside surface only increases slightly as the wall thickness increases.

The dimensionless electroosmotic flow vectors in both the developing and the fully developed region for different channel wall thickness (a) without Joule heating effects (a) $\Delta = 70\mu m$, (b) $\Delta = 150\mu m$ and (c) $\Delta = 200\mu m$ are present in Fig. 6-13. It can be found from Fig. 6-13 that the velocity vector for a thin wall channel (e.g. $\Delta = 70\mu m$) is significantly larger than that for a thick wall channel (e.g. $\Delta = 200\mu m$) due to the higher temperature rise for the thin wall channel (Fig. 6-9). Furthermore, the different temperature variations along flow direction for the channels with different thickness will cause the electroosmotic flow velocity in these channels to exhibit quite different shapes in the developing and the fully-developed region as shown in Fig. 6-13.

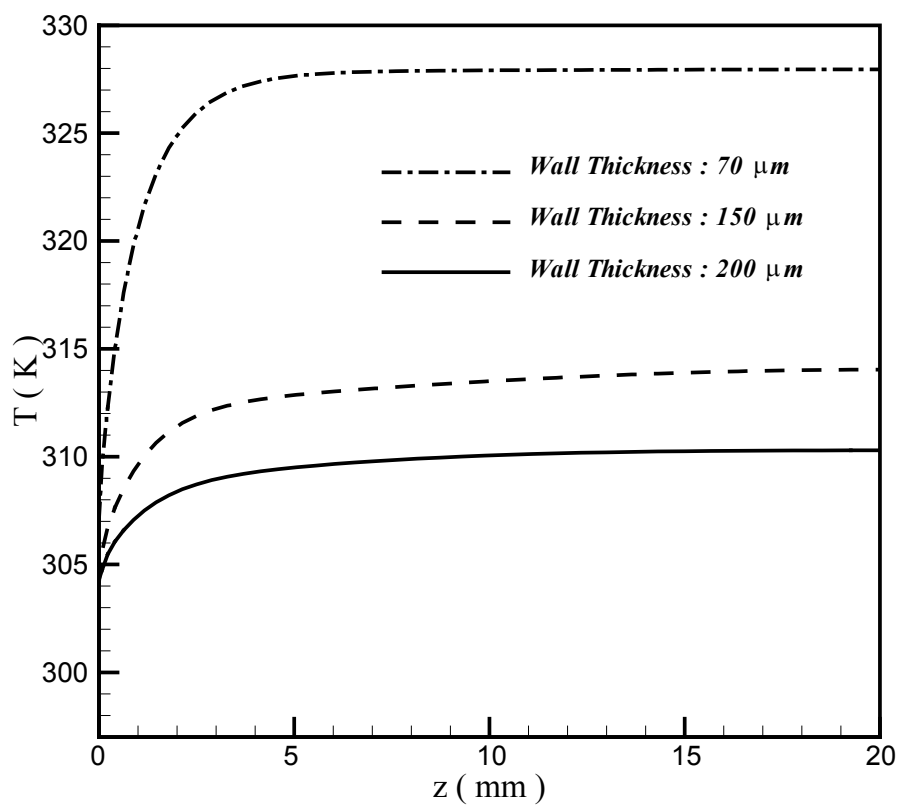
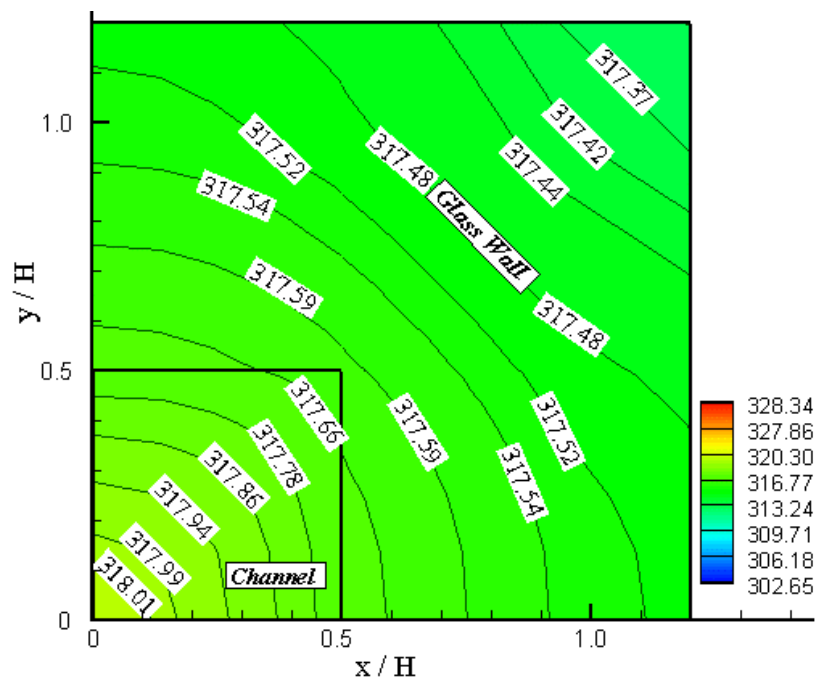
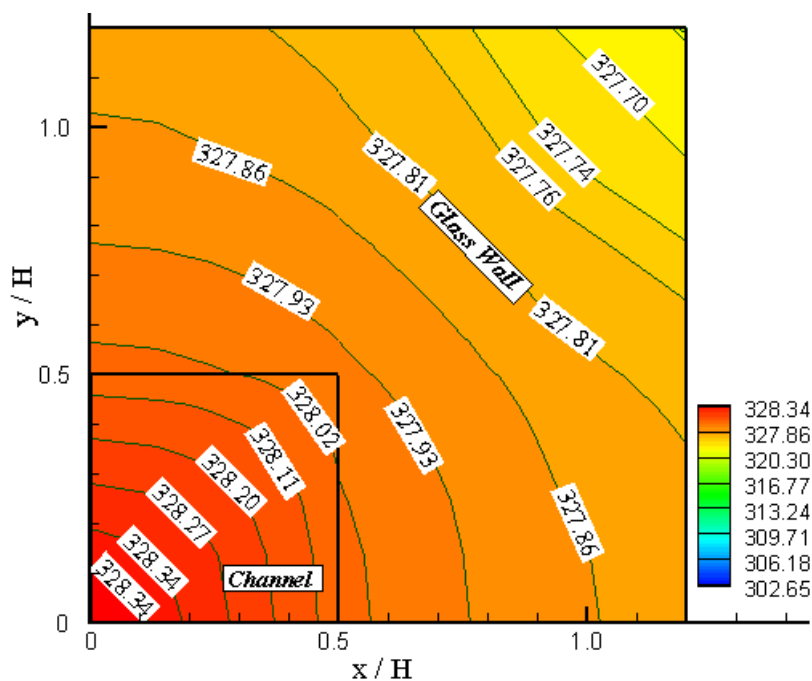


Fig. 6-9 Variation of the liquid temperature at the centerline of the commercial silica glass channel along the flow direction with different wall thickness. Other parameters are: $C = 10^{-2} M$, $k_l = 0.6 W / m K$, $E_0 = 900 V / m$ ($Jo = 0.128$), and $h = 10 W / m^2 K$.

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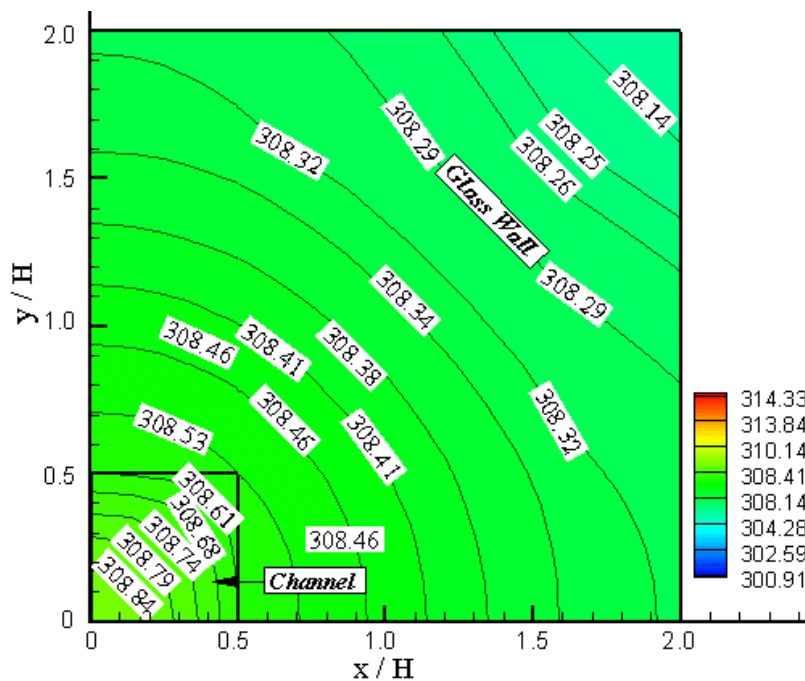


(a)

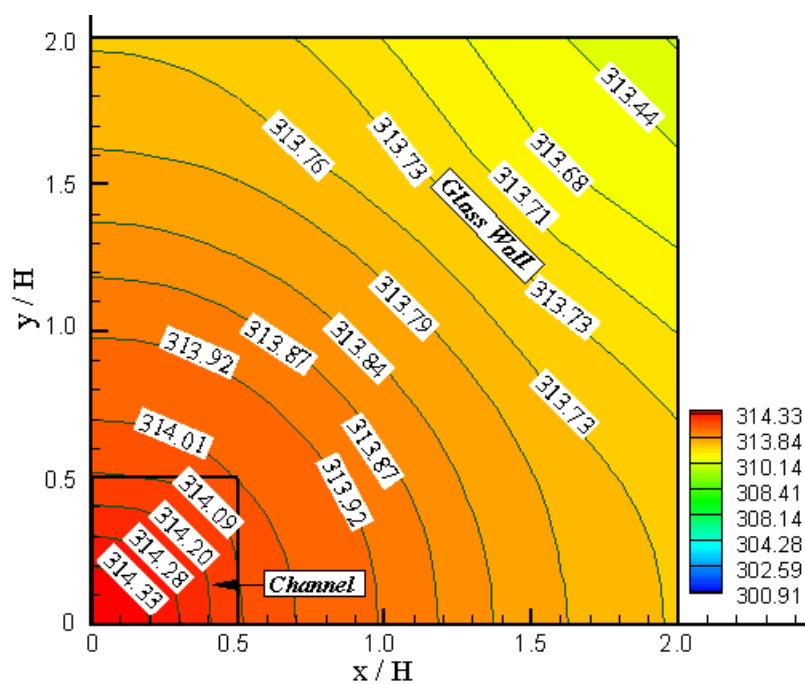


(b)

Fig. 6-10 Transverse cross-sectional temperature contour in both the channel (solution) and the solid wall for a wall thickness of $70\mu\text{m}$, (a) the thermally developing region ($z/H = 10$), and (b) the thermally developed region ($z/H = 178$).

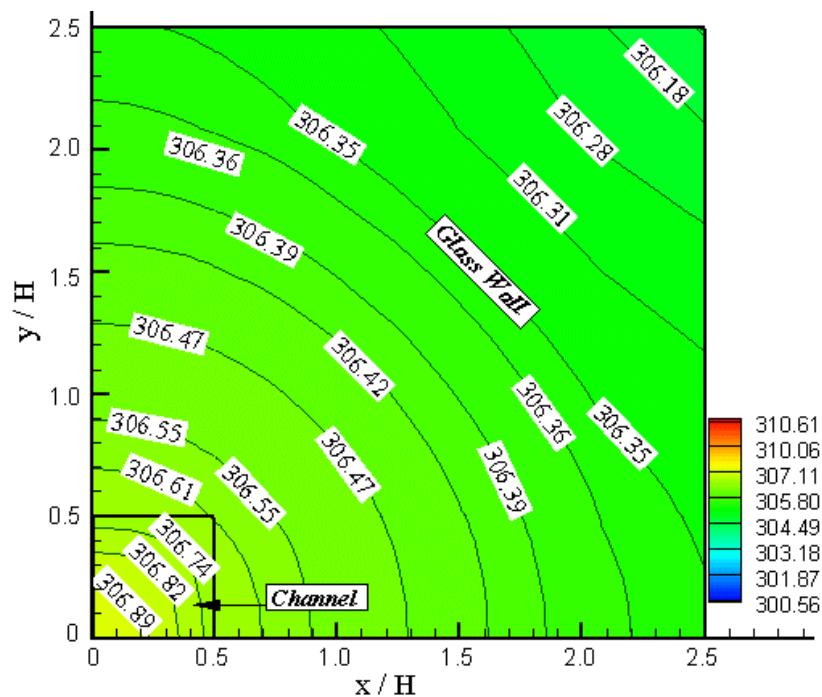


(a)

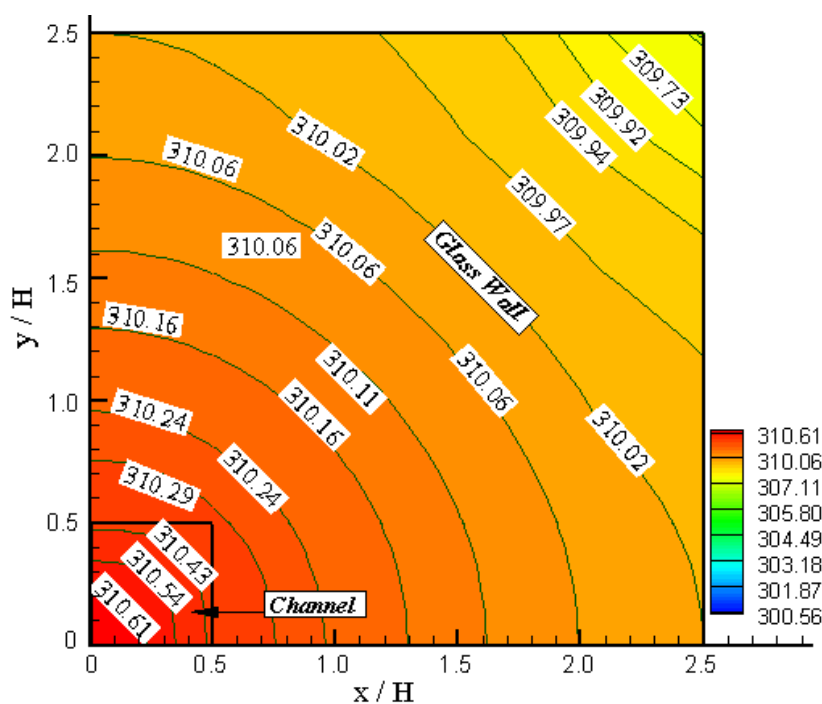


(b)

Fig. 6-11 Transverse cross-sectional temperature contour in both the channel (solution) and the solid wall for a wall thickness of $150\mu\text{m}$, (a) the thermally developing region ($z/H = 10$), and (b) thermally developed region ($z/H = 178$).



(a)



(b)

Fig. 6-12 Transverse cross-sectional temperature contour in both the channel (solution) and the solid wall for a wall thickness of $200\mu m$, (a) the thermally developing region ($z/H = 10$), and (b) thermally developed region ($z/H = 178$)

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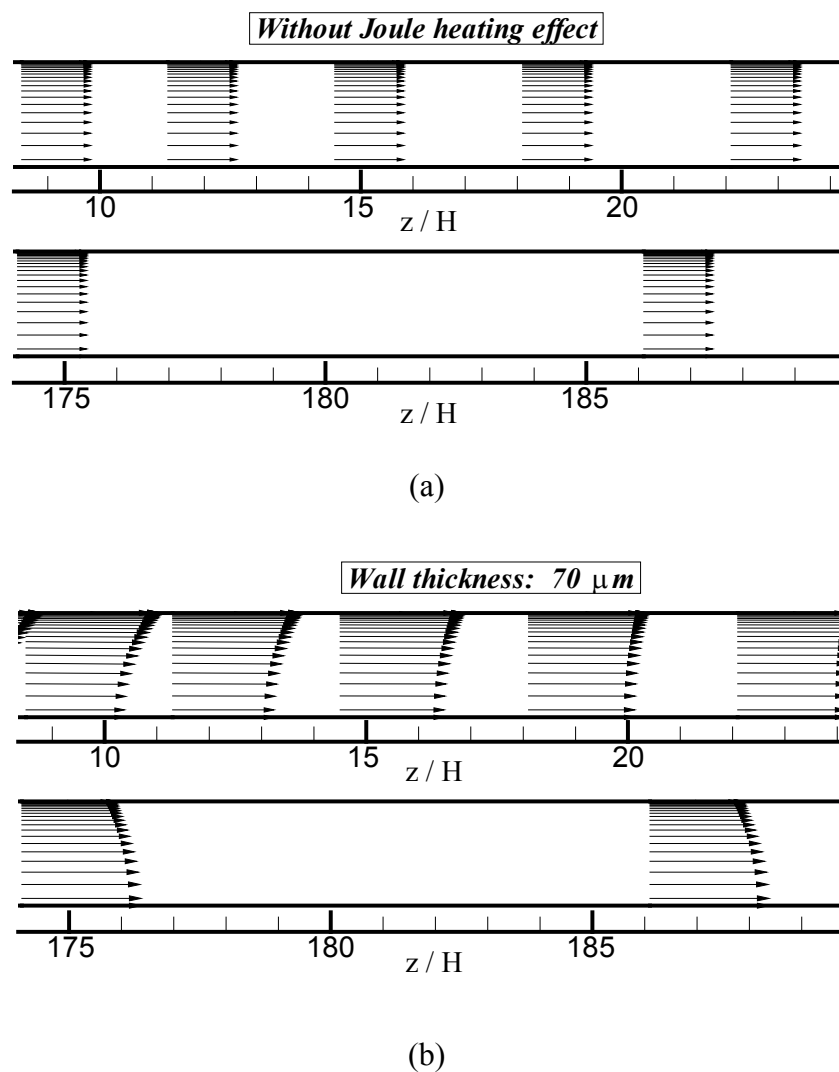


Fig. 6-13 The electroosmotic flow velocity vectors in both the developing and the fully developed regions with different wall thickness: (a) without Joule heating effects; (b) $\Delta = 70 \mu m$.

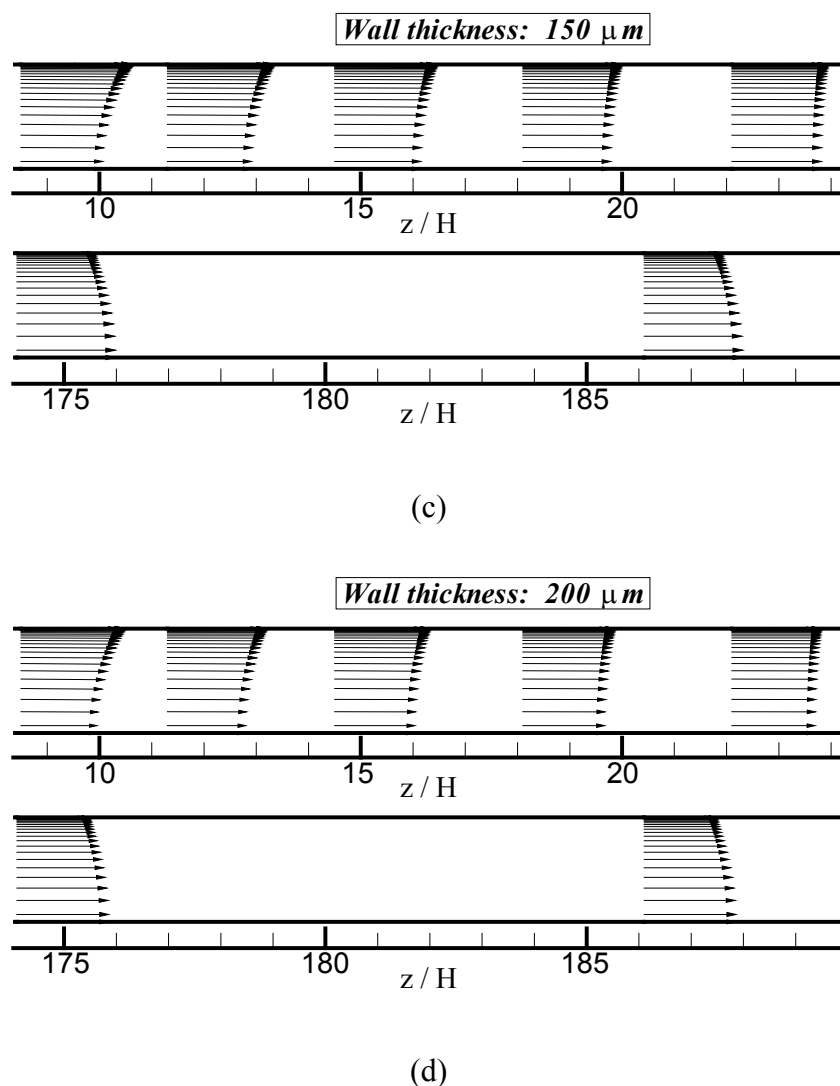


Fig. 6-13 The electroosmotic flow velocity vectors in both the developing and the fully developed regions with different wall thickness: (c) $\Delta = 150 \mu m$ and (d) $\Delta = 200 \mu m$

6.3.2.3 Effect of channel wall material

Due to low cost and simplicity of fabrication, polymer based microfluidic systems have become more and more popular. These polymers typically possess low thermal conductivities which amplify the difficulty in rejecting the internally generated Joule heating. In this section, two fabricated configurations are considered,

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a PDMS/PDMS system (where both substrates are composed of PDMS) and a PDMS/Glass hybrid system (where the bottom substrate is glass and the upper is PDMS) as shown in Fig 6-14, which presents the computation geometry for PDMS/PDMS or PDMS/Glass hybrid microfluidic system. In addition, several sets of chip dimensions are considered in the calculations and they will be described in the following paragraphs.

The variation of the solution temperature at the centerline of the channel along the flow direction for different wall materials is shown in Fig 6-15. The Joule number is 0.057 and the chip dimensions are $240\mu m \times 240\mu m \times 2cm$ for this case. From Fig. 6-15, it is found that the solution temperature for a PDMS/PDMS system is higher than that in a PDMS/Glass system. This indicates that the lower conductivity of PDMS will decrease the heat dissipation through the substrate and hence induce higher solution temperature. While from Fig 6-15, it can be seen that for a channel with such thin substrate, although the material with lower thermal conductivity will induce higher solution temperature, the solution temperature difference between the PDMS/PDMS and the Glass/PDMS channel (less than 0.5 K) is not as significant as compared to the solution temperature increment (around 10 K). This can be explained as follows. Although the PDMS material has low thermal conductivity, the thin substrate gives a relatively low thermal resistance when compared with the high resistance to thermal convection across the outer channel surface to surrounding air. As such, the overall thermal resistance to the whole system has not much difference between the PDMS/PDMS system and the PDMS/Glass system. Therefore, the solution temperature difference between the PDMS/PDMS system and the PDMS/Glass system in this case is insignificant as shown in Fig.6-15.

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Figs. 6-16 and 6-17 give the temperature distributions varying along x , y direction in (a) the thermally developing region and (b) the thermally developed region for a PDMS/Glass system and a PDMS/PDMS system, respectively. Comparing Fig 6-16 with Fig. 6-17, it can be obviously found that due to different thermal conductivities of the PDMS and glass material, the temperature distribution in the PDMS/PDMS system exhibits symmetric character, while the temperature distribution in glass substrate and PDMS substrate for the Glass/PDMS system are quite different. Furthermore, due to the lower thermal conductivity of the PDMS than that of the glass, the heat conduction in the PDMS substrate is lower than that in the glass substrate. Therefore it can be observed from fig 6-16 and Fig 6-17 that at the location having the same distance to the channel center-line, the temperature in the glass substrate is higher than that in the PDMS.

The variation of the solution temperature at the channel centerline along the flow direction for different substrate materials is shown in Fig 6-18. The chip dimensions are $1mm \times 1mm \times 2cm$ and Joule number is 0.285 in this case. The Joule number of 0.285 corresponds to the electrolyte solution with a concentration of $50mM$ and other parameters are identical to those for the Joule number of 0.057. It should be pointed out that in this case, the Joule number is 5 folds to that in the case shown in Figs. 6-15 ~6-17. The chip dimensions are also several times larger than those in above-mentioned case. During our initial numerical test, it is found that on the one hand, using the single-phase model, the solution temperature in channel reaches up to 600K if a Joule number of 0.285 is imposed to the $240\mu m \times 240\mu m \times 2cm$ chip. On the other hand, if the Joule number of 0.057 is imposed to the chip with dimensions of $1mm \times 1mm \times 2cm$, then the increment of the solution temperature in the channel is not significant and the temperature difference

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between the PDMS/PDMS system and the Glass/PDMS system is undistinguishable. As such, the presented cases (different Joule numbers together with different chip dimensions) are chosen to discuss the effect of channel substrate material on the temperature distributions in this section.

From Fig 6-18, it can be found that for the channels with a substrate thickness of 1mm, the thermal conductivity of the substrate has more significant effect on the Joule heating induced channel temperature increment than that of the channel with a substrate thickness of $70\mu m$. This can be explained in the following. For the substrate with such thickness (1mm), the resistance to the heat conduction in the substrate is comparable to that to the heat convection between the substrate and the surrounding. Hence different thermal conductivity of substrate can lead to a large difference of the overall resistance to the heat transfer of the chip system. Thus it leads to a larger difference of the system temperature between the PDMS/Glass and the PDMS/PDMS system as shown in Fig. 6-18. It indicates that the difference of the Joule heating induced solution temperature in the PDMS/PDMS system and the PDMS/Glass system can reach 20K when the increment of the Joule heating induced solution temperature reaches to 80K. On the other hand, since the larger sized chip has larger surface area, the ratio of heat dissipation (through the surface of the chip) to heat generation (the channel volume) in this size chip is much larger than that in the $240\mu m \times 240\mu m \times 2cm$ chip. Hence the Joule number of 0.285, which can cause very high solution temperature in $240\mu m \times 240\mu m \times 2cm$ chip, can cause the solution temperature increment around 80K for the $1mm \times 1mm \times 2cm$ PDMS/PDMS chip and 60 K for the $1mm \times 1mm \times 2cm$ Glass/PDMS chip as shown in Fig. 6-18.

The temperature distributions in both the channel and the substrate along the x, y directions in (a) the thermally developing region and (b) the thermally developed

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region for a PDMS/PDMS chip and a Glass/PDMS chip are respectively presented in Fig. 6-19 and Fig. 6-20. For figures 6-19 and 6-20, the right presents the detailed temperature distributions in and near channel whose area is too small to distinguish in the left.

It can be found that the temperature variation between the channel centerline and the outside of the substrate for this chip is much larger than that of $240\mu\text{m} \times 240\mu\text{m} \times 2\text{cm}$ chip. This is mainly due to the effect of substrate thickness as discussed in the previous paragraph. Furthermore, comparing the temperature distributions in the PDMS/PDMS chip and the Glass/PDMS chip, it can be found that the difference between the channel and the substrate outside surface in the former chip is much larger than that in the latter chip. This can be attributed to the fact that the thermal conductivity of the glass substrate is higher than that of the PDMS substrate as previously mentioned.

Further increasing the chip dimensions to $5\text{mm} \times 1\text{mm} \times 2\text{cm}$ and keeping the Joule number at 0.285, the larger chip surface area causes a larger ratio of the heat dissipation to the heat generation, leading to lower solution temperature (around 40K for a PDMS/PDMS chip and 20K for a Glass/PDMS, as opposed to 80K for PDMS/PDMS chip and 60K for Glass/PDMS with $1\text{mm} \times 1\text{mm} \times 2\text{cm}$ chip) as shown in Fig.6-21. Fig. 6-21 presents the variation of the solution temperature at the channel centerline along the flow direction with different substrate material for a $5\text{mm} \times 1\text{mm} \times 2\text{cm}$ chip. From Fig.6-21, it can also be observed that although the solution temperature in the $5\text{mm} \times 1\text{mm} \times 2\text{cm}$ chip decreases significantly (40K) as compared with that in the $1\text{mm} \times 1\text{mm} \times 2\text{cm}$ chip. The difference of solution temperature between the PDMS/PDMS chip and the Glass/PDMS chip does not decrease with the chip dimensions. This can be explained as follows. As discussed

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earlier, the proportion between the resistance to heat conduction in the substrate and the overall resistance to the whole system increases with increasing the substrate thickness. Therefore, the difference of the resistance to heat conduction in different substrates with different thermal conductivities also increases with the increase of the substrate thickness. Hence if overall solution temperature increment remains unchanged, the difference of the solution temperature between the PDMS/PDMS chip and the Glass/PDMS chip tends to increase with increasing substrate thickness. However, in this case, the overall solution temperature increment decreases with increasing substrate thickness due to the increase in the outside surface area. Therefore, the difference of solution temperature between the PDMS/PDMS chip and the Glass/PDMS chip varies from case to case (decrease, increase or keep unchanged), depending on other parameters and conditions.

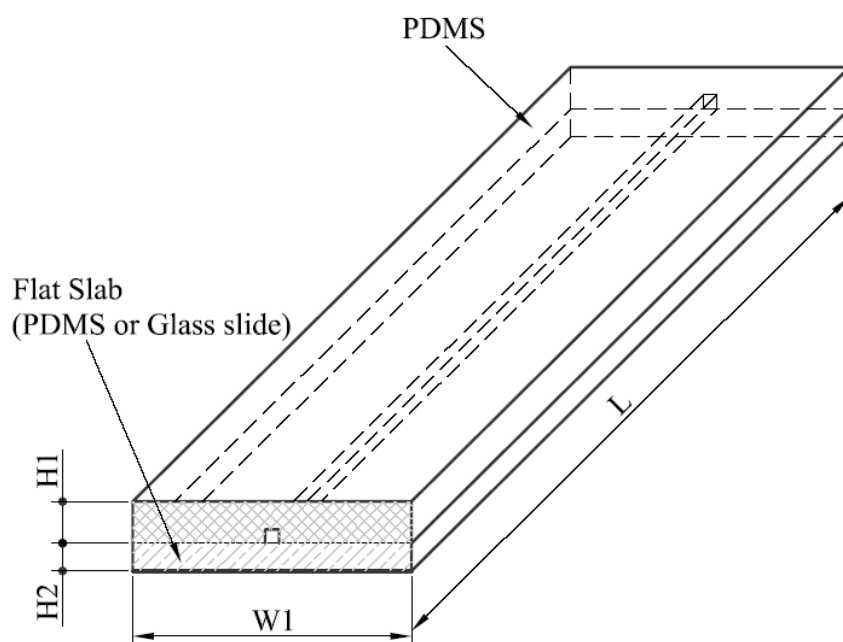


Fig. 6-14 Computation geometry for a PDMS/PDMS or a Glass/PDMS hybrid microfluidic channel

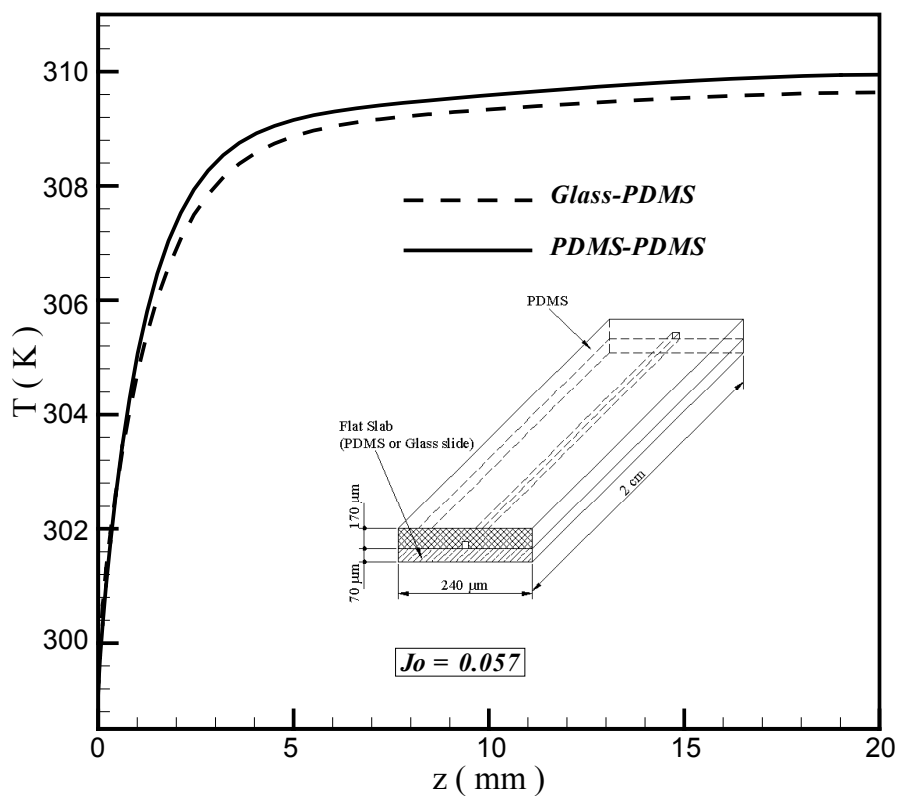


Fig. 6-15 Variation of the liquid temperature at the centerline of the channel along the flow direction with different wall materials for a Joule number of 0.057. The chip dimensions are shown in the figure.

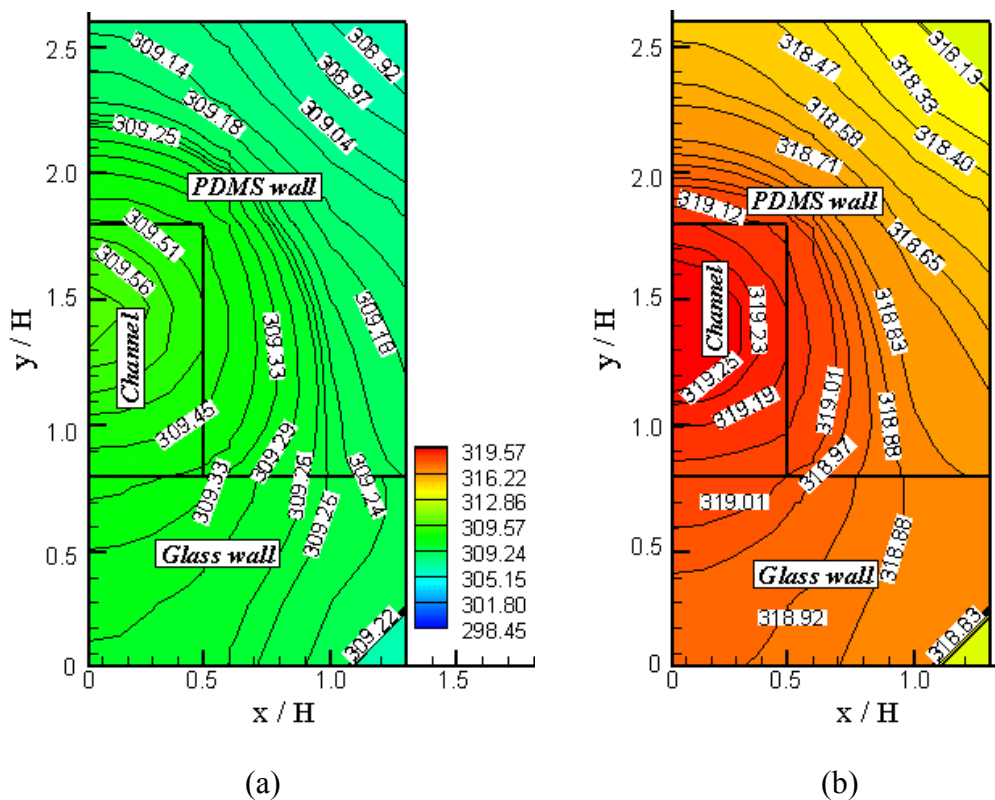


Fig. 6-16 Transverse cross-sectional temperature contour in both the channel (solution) and the solid wall for a Glass/PDMS hybrid system with a Joule number of 0.057: (a) the thermally developing region ($z/H = 10$); (b) thermally developed region ($z/H = 178$). The chip dimensions are shown in Fig. 6-15.

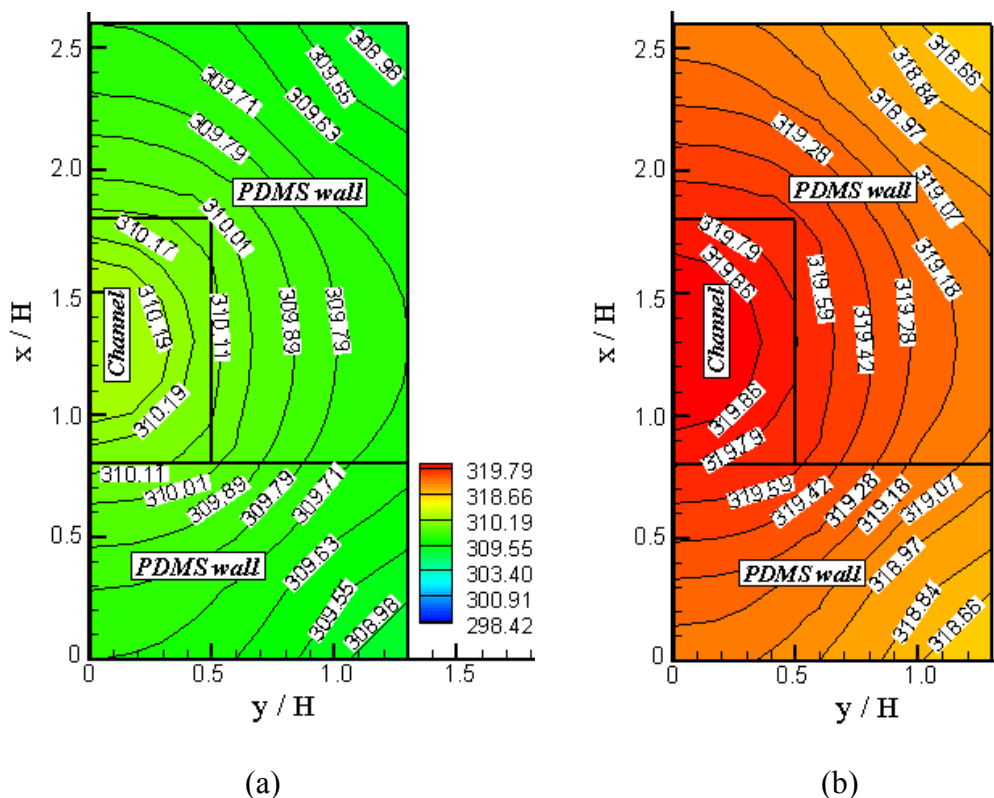


Fig. 6-17 Transverse cross-sectional temperature contour in both the channel (solution) and the solid wall for a PDMS/PDMS system with a Joule number of 0.057: (a) the thermally developing region ($z/H = 10$); (b) thermally developed region ($z/H = 178$). The chip dimensions are shown in Fig. 6-15.

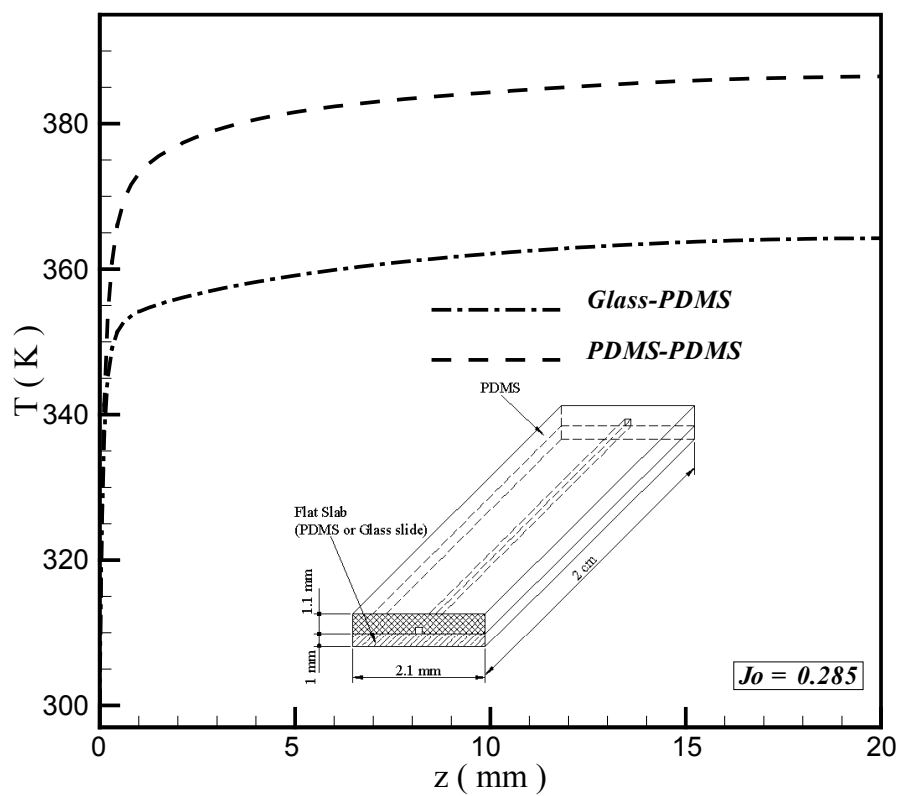


Fig. 6-18 Variation of the liquid temperature at the centerline of the channel along the flow direction with different wall materials for a Joule number of 0.285. The chip dimensions are shown in the figure.

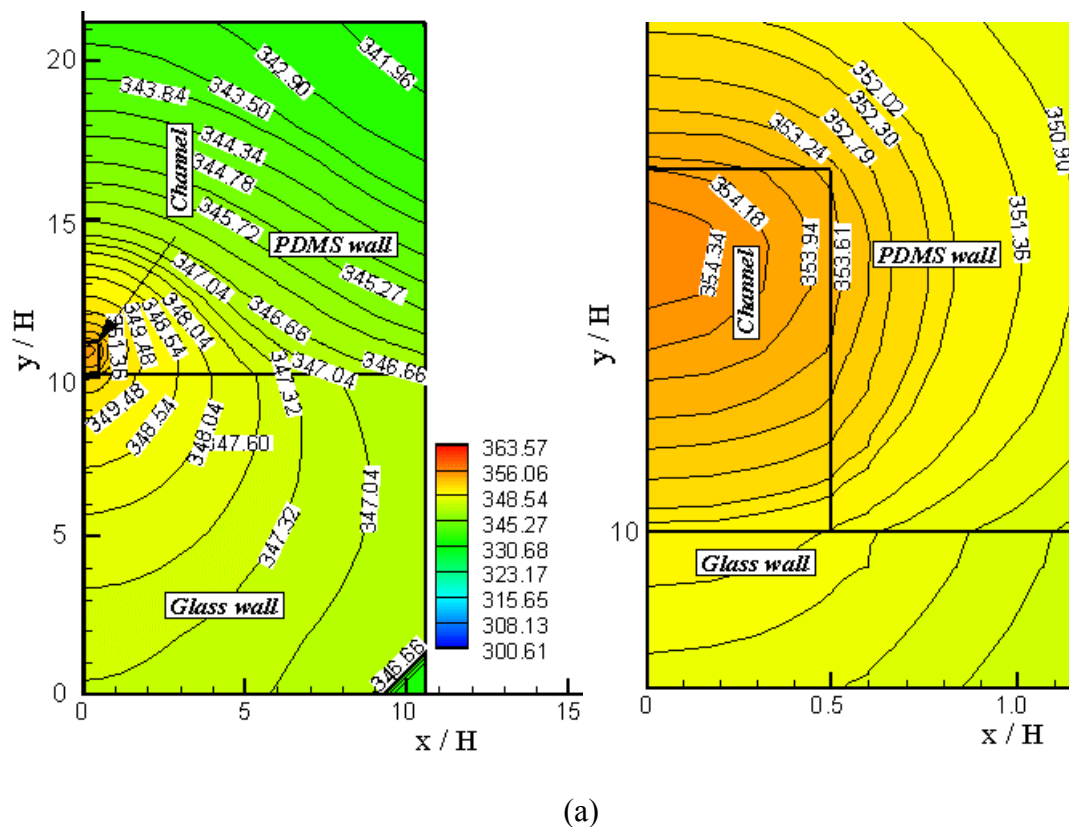
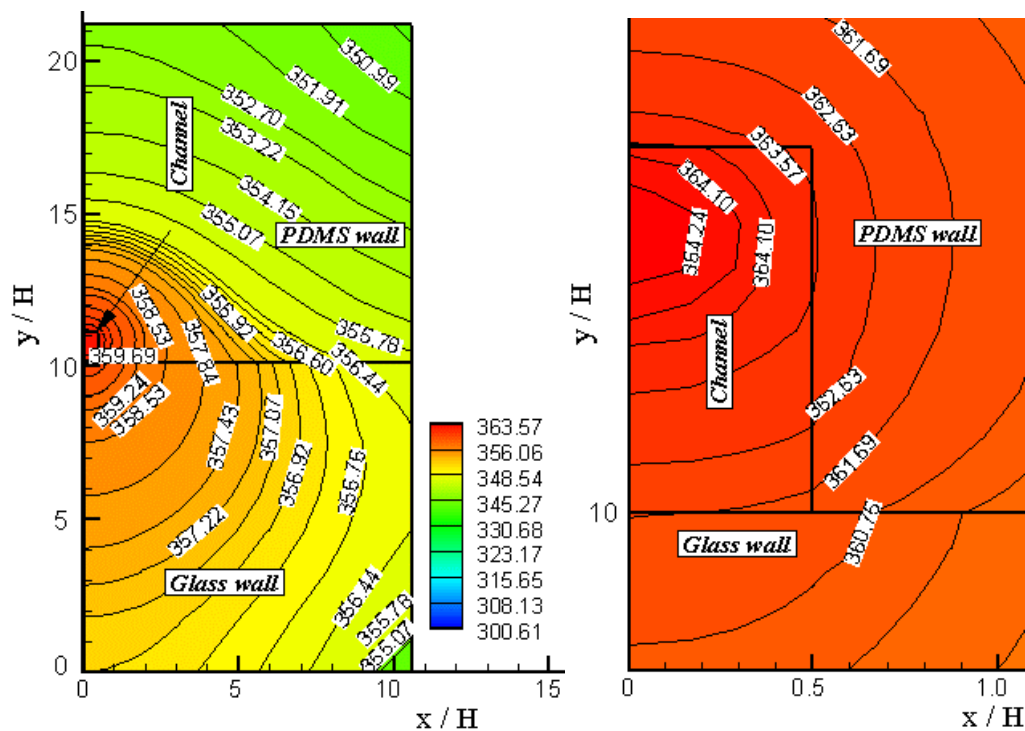
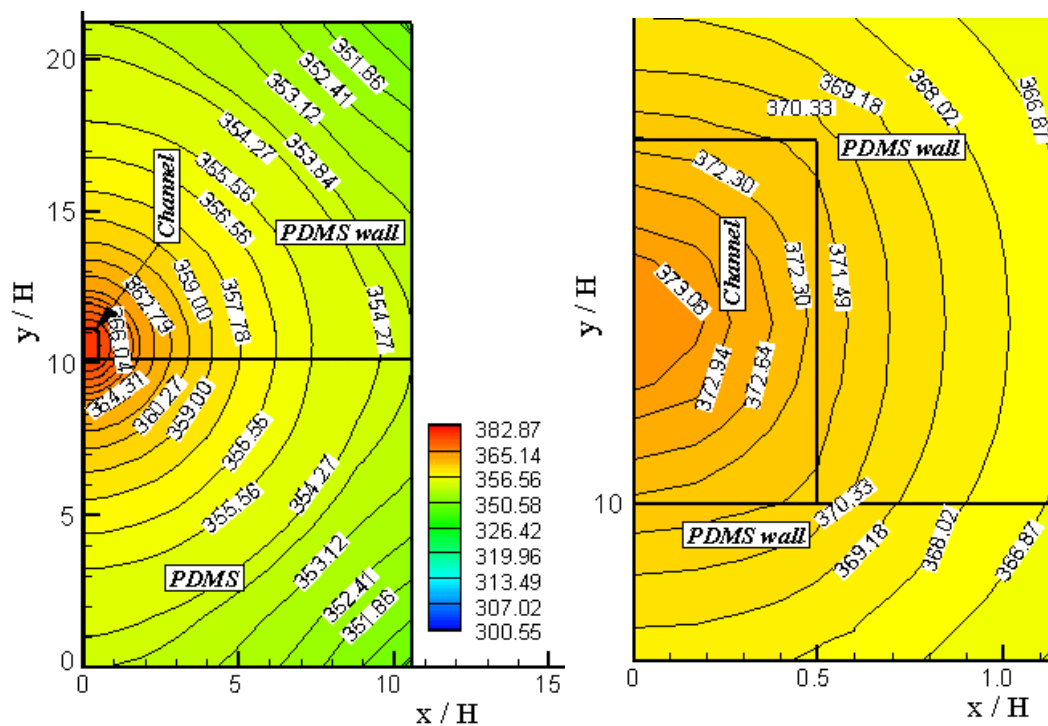


Fig. 6-19 Transverse cross-sectional temperature contour in both the channel (solution) and the solid wall for a Glass/PDMS hybrid system with a Joule number of 0.285: (a) the thermally developing region ($z/H = 10$). The chip dimensions are shown in Fig.6-18.



(b)

Fig. 6-19 Transverse cross-sectional temperature contour in both the channel (solution) and the solid wall for a Glass/PDMS hybrid system with a Joule number of 0.285: (b) the thermally developed region ($z/H = 178$). The chip dimensions are shown in Fig.6-18.



(a)

Fig. 6-20 Transverse cross-sectional temperature contour in both the channel (solution) and the solid wall for a PDMS/PDMS system with a Joule number of 0.285: (a) the thermally developing region ($z/H = 10$). The chip dimensions are shown in Fig. 6-18.

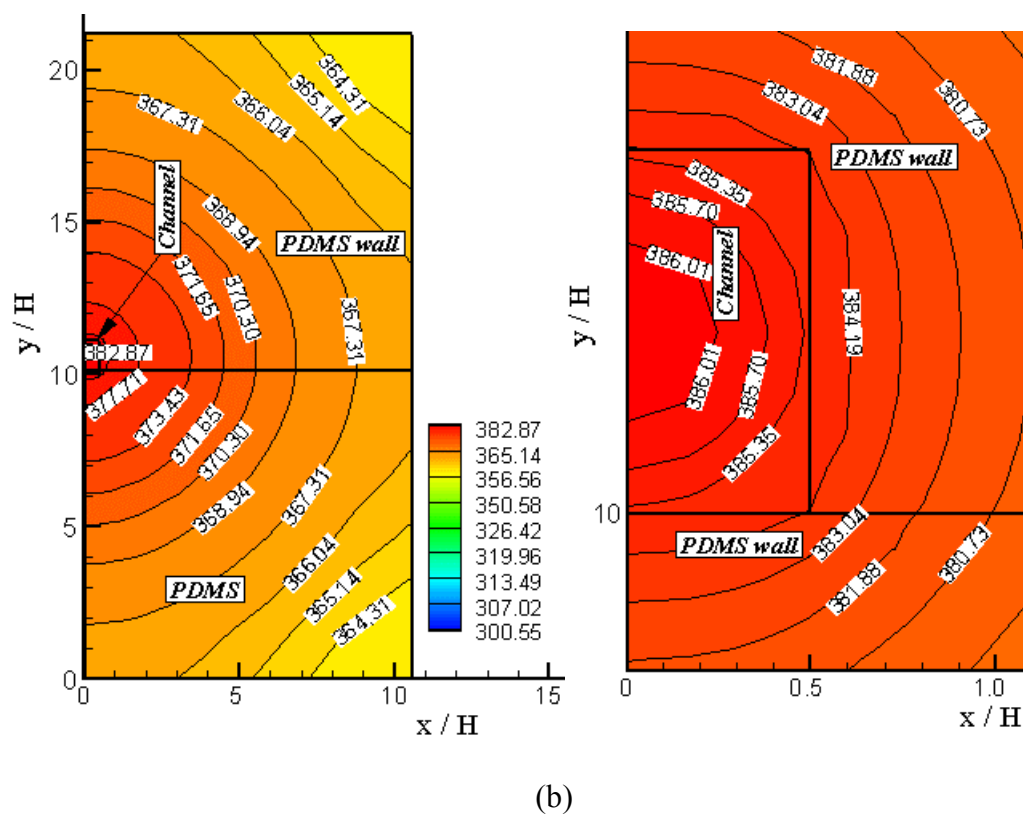


Fig. 6-20 Transverse cross-sectional temperature contour in both the channel (solution) and the solid wall for a PDMS/PDMS system with a Joule number of 0.285: (b) the thermally developed region ($z/H = 178$). The chip dimensions are shown in Fig. 6-18.

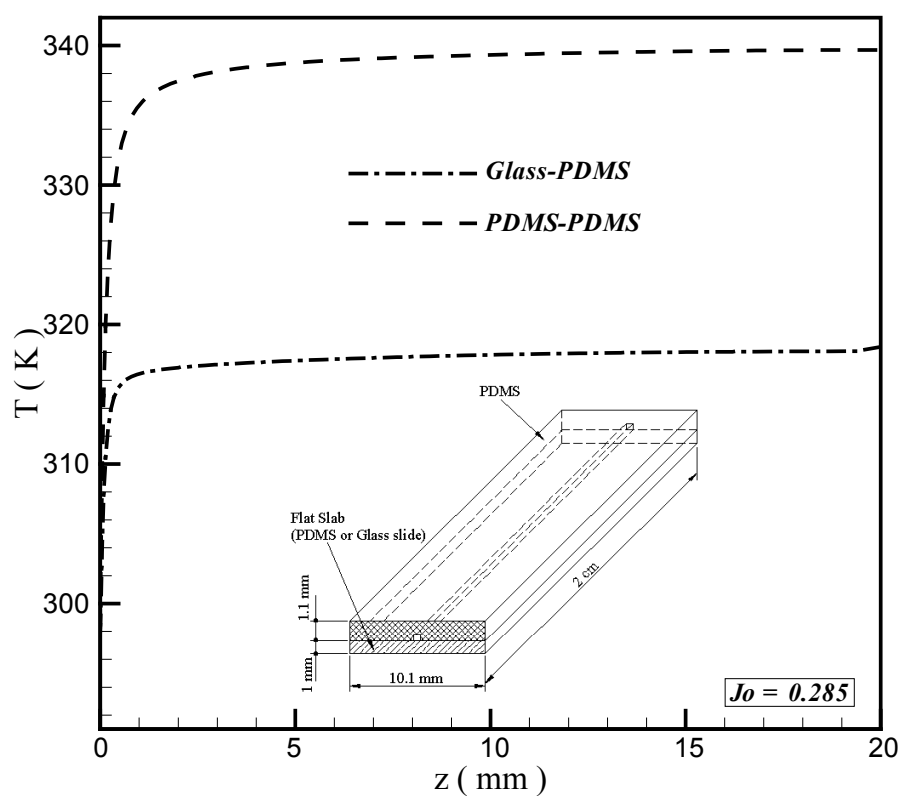


Fig. 6-21 Variation of the liquid temperature at the centerline of the channel along the flow direction with different wall materials for a Joule number of 0.285. The chip dimensions are shown in the figure.

6.3.3 Joule heating effect on sample band transport

In this section, the Joule heating effects on the sample species with a controlled mass transported in a Glass/PDMS system and a PDMS/PDMS system are discussed.

The simulation results for the dispersion of a finite sample plug in a Glass/PDMS and PDMS/PDMS system are shown in Fig. 6-22. In this case, the chip dimensions are $5\text{mm} \times 1\text{mm} \times 2\text{cm}$ and the Joule number is 0.285. In the absence of Joule heating, it is seen that the difference of sample band transported in these two systems is undistinguished. This should be expected because the difference of electroosmotic mobility between these two systems at room temperature is not significant (Ross *et al.*, 2001). The electroosmotic flow velocity for these two systems can be regarded as the same, and hence, the sample band transported in these two systems exhibits the same features. However, in the presence of Joule heating, it is clearly shown that the difference of sample band transported in these two systems is significant. As discussed in previous sections, the liquid solution temperature increment in the PDMS/PDMS system is higher than that in the Glass/PDMS system, and the solution temperature elevation leads to reduced solution viscosity and electrical conductivity and increased EOF velocity, and the diffusivity of the sample species, thus making the sample band move faster and exhibit lower peak and broader width in the PDMS/PDMS system. Furthermore, it can also be observed from Fig. 6-22 that transport of a finite sample plug in a PDMS/PDMS system causes a more significant distortion of the sample band from its plug-like shape than that in a Glass/PDMS system. This is due to the liquid solution temperature gradient along the flow direction in the PDMS/PDMS system being larger than that in the Glass/PDMS system as shown in Fig. 6-21. As a result, based on the previous discussion, a larger inner pressure gradient is induced in the PDMS/PDMS system than that in the

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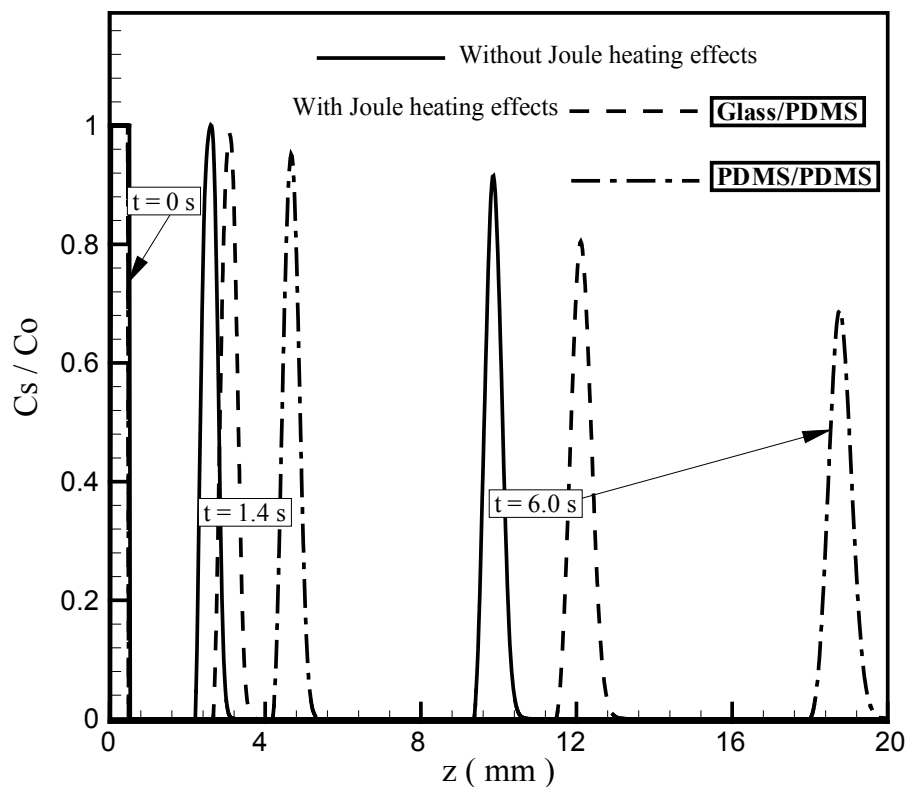
Glass/PDMS system, hence a more distorted electroosmotic flow velocity profile will be generated in the PDMS/PDMS system than that in the Glass/PDMS system. Meanwhile, the transverse solution temperature variation (i.e. along the x, y directions) is negligible as compared to the solution temperature increment along the channel.

In addition, by comparing the results in Fig. 6-22 with those in Fig. 5-23, it can be found that transport of a finite sample plug in the fabricated PDMS/PDMS or Glass/PDMS system are quite different from that in a commercial capillary electrophoresis system discussed in Chapter 5. The sample band in the capillary electrophoresis system exhibits a concave shape in the entire capillary, while in the fabricated PDMS/PDMS or Glass/PDMS system, the sample band exhibits a concave shape in the developing region and a convex shape in the fully developed region. This scenario can be explained as follows. As previously discussed, the induced positive pressure gradient in the developing region can generate a concave velocity profile and the induced negative pressure gradient in the developed region can generate a convex velocity profile for both the capillary electrophoresis system with the special thermostated cooling mode and the fabricated PDMS/PDMS and Glass/PDMS microfluidic systems with the free air convection cooling mode. However, for the capillary electrophoresis system, the radial solution temperature variation is significant, leading to significant sample species electrophoresis velocity gradient along the radial direction with the largest electrophoresis velocity located at the capillary center due to the highest temperature. As the direction of the electrophoresis velocity for negatively charged samples (e.g., DNA species) is opposite to electroosmosis velocity, the sample species in the central region transports slower than that close to the wall region resulting in a concave sample band shape as shown in Fig 5-23. In the contrary, as mentioned earlier, the transverse solution temperature

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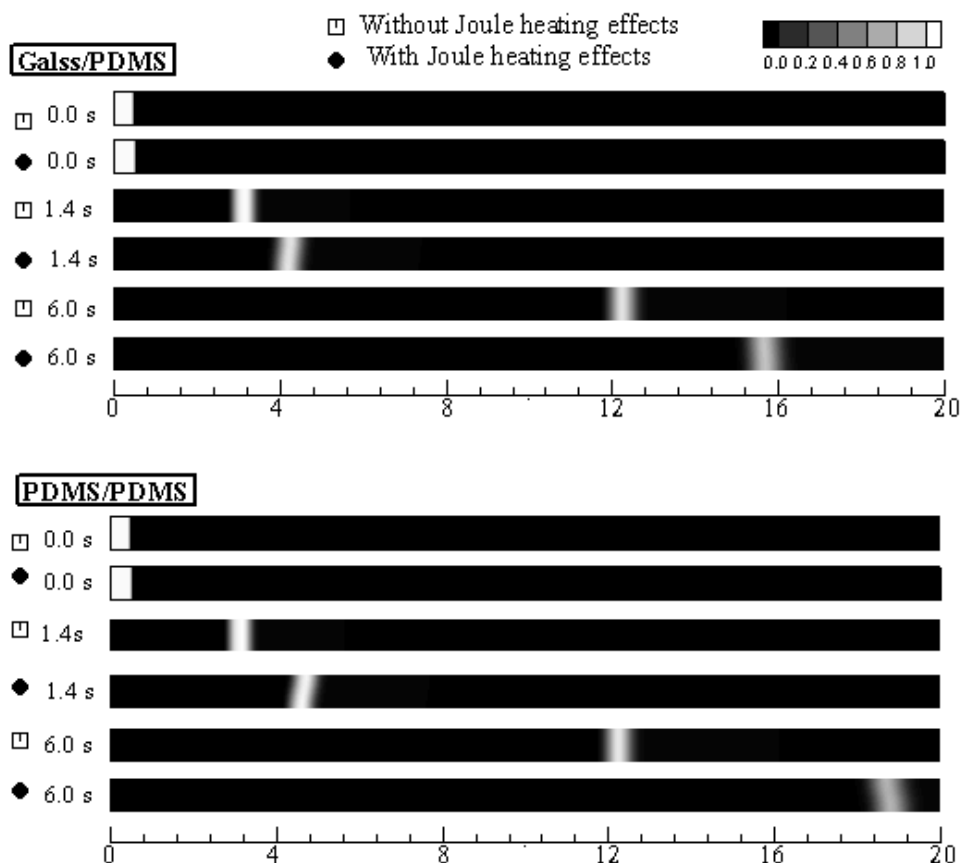
variation (i.e. along the x, y directions) in the fabricated PDMS/PDMS and Glass/PDMS microfluidic systems is negligible as compared to the axial solution temperature increment. As a result, the electrophoretic velocity of sample species is uniform along the transverse direction and the sample band follows the same shape as the electroosmotic velocity profiles as shown Fig. 6-22, namely, a concave shape in developing region and a convex shape in the developed region.

Fig. 6-23 shows the numerical simulations of the Joule heating effects on the dispersion of a finite sample plug which contains three different kinds of sample species including (i) negatively charged sample #1 ($\mu_{ep0} = -1.0 \times 10^{-8} \text{ m}^2 / \text{V s}$), (ii) neutrally charged sample #2 $\mu_{ep0} = 0 \text{ m}^2 / \text{V s}$, and (iii) positively charged sample #3 ($\mu_{ep0} = 1.0 \times 10^{-8} \text{ m}^2 / \text{V s}$). It is noted that despite different electrophoretic mobilities, the sample band essentially exhibits the same shape and the difference only lies in the transport speed of sample band. This is because in the calculation, it is assumed that both the mass diffusion coefficient and the electrophoretic velocities of the three sample species have the same correlations with solution temperature. Consequently, under the same flow conditions, the presence of Joule heating exhibits the same effects as discussed earlier on the peak and width of the sample band. Moreover, as indicated in Eq. (6-7) which governs the sample mass transport, the sample band transport is the linear superposition of the electroosmotic flow velocity and the electrophoretic velocity of sample species. As a result, the sample band transport takes (decreasing) order of the positively charged sample #3 > the neutrally charged sample #2 > the negatively charged sample #1.



(a)

Fig. 6-22 Simulation results of the Joule heating effects on the dispersion of a finite sample plug for a Glass/PDMS system and a PDMS/PDMS system: (a) axial variation of the cross-sectional average of the sample concentration. The parameters are: $C = 50mM$ ($Jo = 0.285$), $E_0 = 600V/cm$, $\zeta = -50mV$, $D_0 = 2.01 \times 10^{-10} m^2/s$ and $\mu_{ep0} = -1.0 \times 10^{-8} m^2/Vs$.



(b)

Fig. 6-22 Simulation results of the Joule heating effects on the dispersion of a finite sample plug for a Glass/PDMS system and a PDMS/PDMS system: (b) time evolution of the sample shape in the upper-half microchannel. The parameters are: $C = 50mM$ ($Jo = 0.285$), $E_0 = 600V/cm$, $\zeta = -50mV$, $D_0 = 2.01 \times 10^{-10} m^2/s$ and $\mu_{ep0} = -1.0 \times 10^{-8} m^2/Vs$.

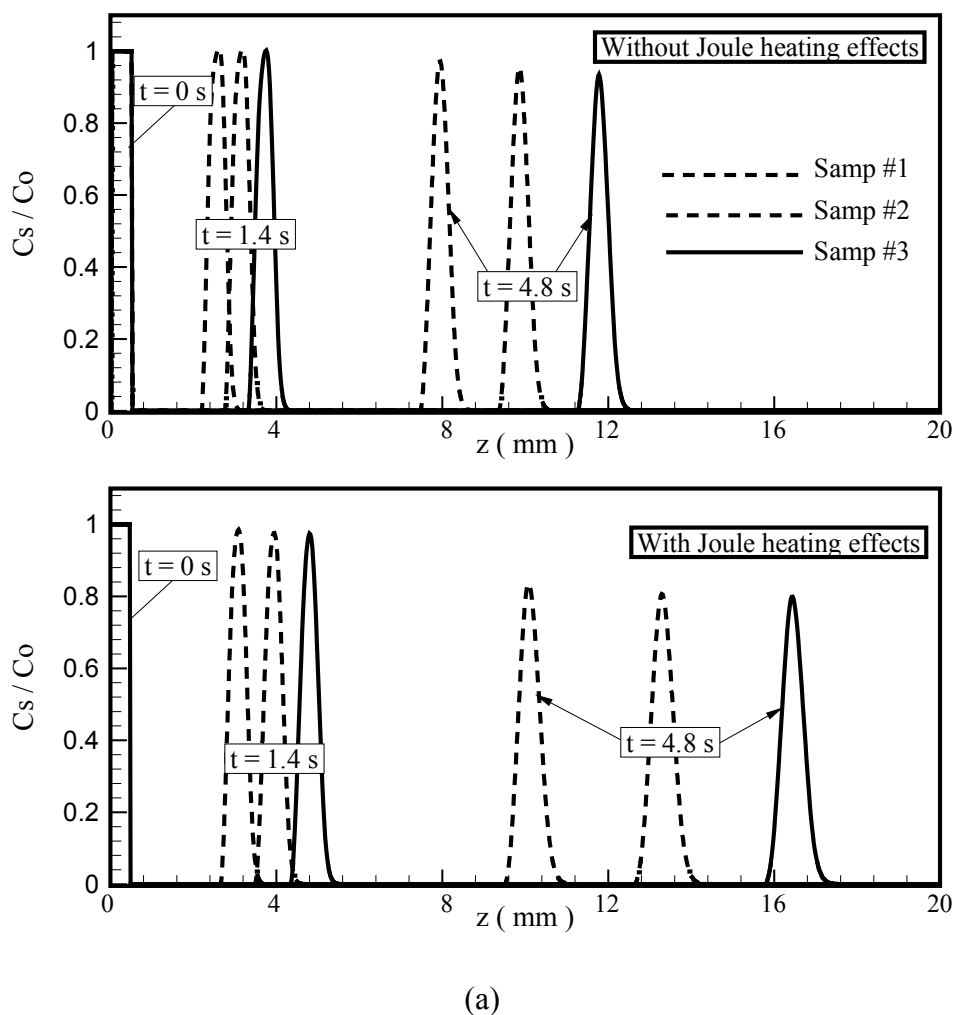


Fig. 6-23 Simulation results of the Joule heating effects on the dispersion of a finite sample plug for different electrophoretic mobilities of the sample species in a Glass/PDMS system: (a) axial variation of the cross-sectional average of the sample concentration. The parameters are: $C = 50\text{mM}$ ($Jo = 0.285$), $E_0 = 600\text{ V/cm}$, $\zeta = -50\text{mV}$, $D_0 = 2.01 \times 10^{-10}\text{ m}^2/\text{s}$, $\mu_{ep0} = -1.0 \times 10^{-8}\text{ m}^2/\text{V} \cdot \text{s}$ (#1), $\mu_{ep0} = 0$ (#2), and $\mu_{ep0} = 1.0 \times 10^{-8}\text{ m}^2/\text{V} \cdot \text{s}$ (#3)

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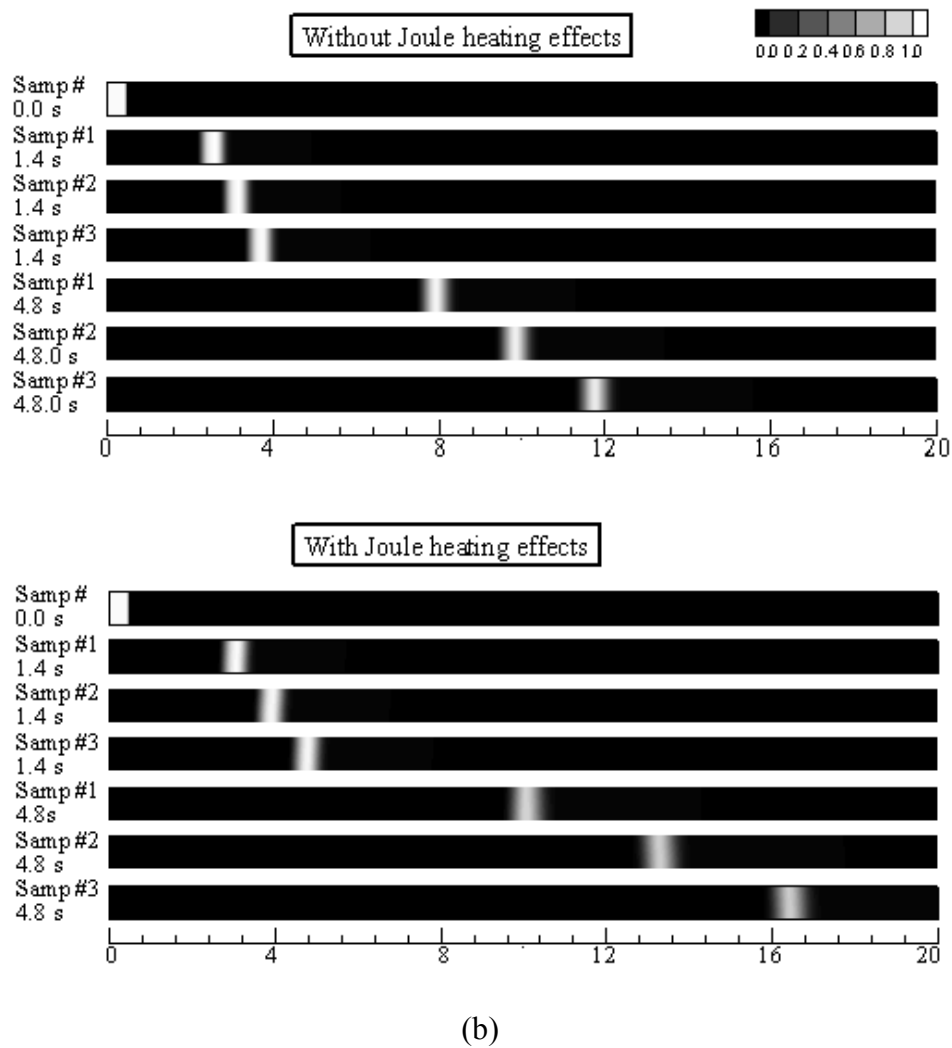


Fig. 6-23 Simulation results of the Joule heating effects on the dispersion of a finite sample plug for different electrophoretic mobilities of the sample species in a Glass/PDMS system: (b) time evolution of the sample shape distributions in the upper-half microchannel. The parameters are: $C = 50mM$ ($Jo = 0.285$), $E_0 = 600 V/cm$, $\zeta = -50mV$, $D_0 = 2.01 \times 10^{-10} m^2/s$, $\mu_{ep0} = -1.0 \times 10^{-8} m^2/V \cdot s$ (#1), $\mu_{ep0} = 0$ (#2), and $\mu_{ep0} = 1.0 \times 10^{-8} m^2/V \cdot s$ (#3)

6.4 Joule heating and its effects on electrokinetic mixing in T-shape channels

Microfluidics mixing is one of important techniques in biotechnology. Electrokinetic mixing is widely used in microfluidic system, and numerous studies on electrokinetic mixing without considering Joule heating effects have been reported in the literature (*Ermakov et al.*, 1998; *Ericckson and Li*, 2002). Fig. 6-24 presents the schematic diagram of a basic geometry for microfluidic mixing in T-shape channels. For low Reynolds number electroosmotically driven flows in microfluidic devices, species mixing is inherently diffusion dominated. The species diffusion depends on the diffusion coefficient, which is a temperature dependant parameter. Therefore, the Joule heating effects on the sample species mixing will be studied in this section.

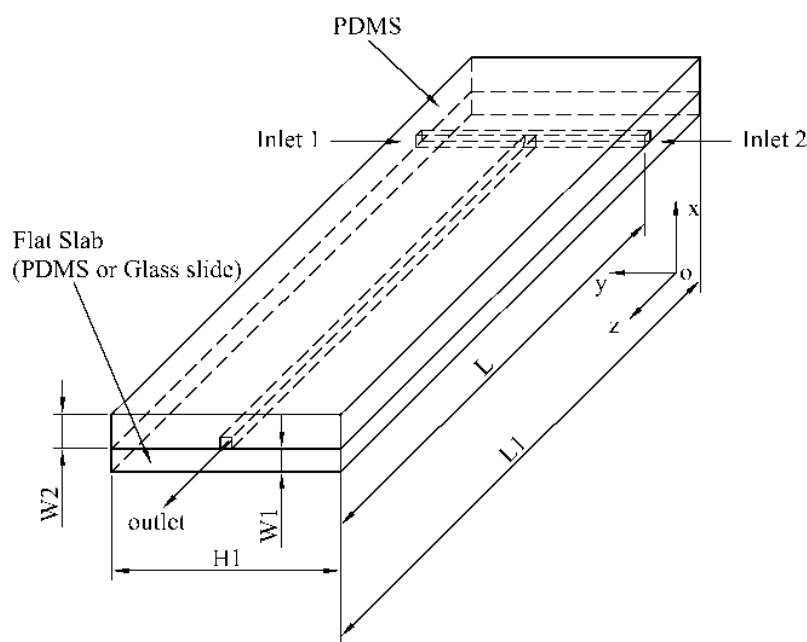


Fig. 6-24 Schematic diagram of geometry for sample species mixing in T-shape channels

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6.4.1 Boundary conditions

For electrokinetic mixing in T-shape channels as shown in Fig. 6-24, the governing equations are the same as those presented in equations (6-1) –(6-19) and the boundary condition can be expressed as:

At the Inlet 1 and 2

$$\bar{T} = 1.0 \quad \bar{\psi} = 0 \quad \bar{\phi} = 1.0 \quad \bar{u} = 0 \quad \frac{\partial \bar{v}}{\partial y} = 0 \quad \bar{w} = 0 \quad (6-23a)$$

At the outlet

$$\frac{\partial \bar{T}^2}{\partial z^2} = 0 \quad \frac{\partial \bar{\psi}}{\partial z} = 0 \quad \bar{\phi} = 0.0 \quad \frac{\partial \bar{u}}{\partial z} = 0 \quad \frac{\partial \bar{v}}{\partial z} = 0 \quad \frac{\partial \bar{w}}{\partial z} = 0 \quad (6-23b)$$

At all channel wall inside surfaces, the no-slip boundary conditions are applied to the velocity field (N-S equation), the fixed zeta potentials are imposed to the electrical double layer potential field (Poisson-Boltzmann equation), and the insulation boundary conditions are assigned to the applied electric field (Laplace equation), namely

$$\bar{u} = 0 \quad \bar{v} = 0 \quad \bar{w} = 0 \quad \bar{\psi} = \bar{\zeta} \quad \frac{\partial \bar{\phi}}{\partial x} = 0 \quad \frac{\partial \bar{\phi}}{\partial y} = 0 \quad \frac{\partial \bar{\phi}}{\partial z} = 0 \quad (6-23c)$$

Since the energy equation is solved together with the conjugated heat conduction equation, the third kind boundary conditions (i.e. natural convection heat transfer with surrounding air) are imposed the temperature field at all the outside surface of the fabricated microchip, namely

$$-\bar{k}_s \left. \frac{\partial \bar{T}}{\partial x} \right|_{\text{outersurface}} = \frac{hH}{k_{ref}} (\bar{T} - 1) \quad (6-24a)$$

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$$-\bar{k}_s \left. \frac{\partial \bar{T}}{\partial y} \right|_{\text{outersurface}} = \frac{hH}{k_{ref}} (\bar{T} - 1) \quad (6-24b)$$

$$-\bar{k}_s \left. \frac{\partial \bar{T}}{\partial z} \right|_{\text{outersurface}} = \frac{hH}{k_{ref}} (\bar{T} - 1) \quad (6-24c)$$

In this section, we consider the case of a stream with sample species concentration

$C_s = C_0$ mixing with another stream with sample species concentration $C_s = \frac{C_0}{2}$.

Thus the fixed conditions assigned to the inlet1 ($\bar{C}_s = 1.0$) and inlet 2 ($\bar{C}_s = 0.5$).

Same as previous sections, the outlet boundary condition are assigned as:

$$\frac{\partial^2 \bar{C}_s}{\partial z^2} = 0 \quad (6-25a)$$

At the channel wall inner surfaces, the impermeable conditions are imposed for the sample species, namely

$$\frac{\partial \bar{C}_s}{\partial x} = 0 \quad \frac{\partial \bar{C}_s}{\partial y} = 0 \quad \frac{\partial \bar{C}_s}{\partial z} = 0 \quad (6-25b)$$

The microchannels in the calculations have a cross-section of $100\mu m \times 100\mu m$, the chip geometry is shown in Fig. 6-22 and its dimensions are: $H_1 = 1cm$, $W_1 = 1mm$, $W_2 = 1.5mm$, $L_1 = 1.5cm$, and $L = 1.0cm$. The sample carrier is $NaHCO_3$ electrolyte and its properties are considered to be the same as water: density $\rho = 998kg/m^3$, thermal capacity $4180kJ/kg K$ and thermal conductivity $k_l = 0.6W/m K$ (at room temperature $298K$). The electric conductivity for $NaHCO_3$ solution is $\lambda_{+0} = 50.08 \times 10^{-4} m^2 S/mol$ (Na^+) and $\lambda_{-0} = 44.5 \times 10^{-4} m^2 S/mol$ (HCO_3^-) (at room temperature $298K$) (Weast, et al., 1986). A fluorescein dye is chosen as the sample species to be mixed in the system, and its mass diffusivity and electrophoretic

mobility (at 298K) are $D_0 = 4.37 \times 10^{-10} m^2 / s$ and $\mu_{ep0} = 2.04 \times 10^{-8} m^2 / V s$, respectively (Paul et al., 1998).

6.4.2 Joule heating induced temperature field

Fig. 6-25 and Fig.6-26 respectively present the detailed comparison of the temperature distributions in the PDMS/ PDMS chip system with those in the Glass/PDMS chip system for two different Joule numbers, 0.089 and 0.285. The two figures include (a) the temperature contour of the system surface, (b) the temperature distributions around the T-shape channel in the substrate (c) the detailed temperature contour near the T-section on the T channel plane (i.e. y-z plane), (d) variation of the solution temperature at the centerline of the mixing channel along the flow direction, (e) the detailed temperature distributions near the T section on the plane perpendicular to the T-channel (i.e., x-z plane along the channel deep direction), and (f) the temperature distribution varying along x, y direction in thermally developed region. The Joule number of 0.089 and 0.285 respectively corresponds to the parameters as: $E_0 = 750V / cm$, $C = 10mM$ for $J = 0.089$ and $E_0 = 600V / cm$, $C = 50mM$ for $J = 0.285$.

By comparing Fig. 6-25 with Fig. 6-26, it is can be found that for such size chip system, the glass substrate can significantly improve the heat dissipation of the chip as compared to the PDMS substrate. According to the discussion presented in previous sections, this can be attributed to the much higher thermal conductivity of the glass substrate than that of the PDMS substrate. As a result, the Glass/PDMS chip system can lead to much lower solution temperature than that of the PDMS/PDMS chip system as shown in Fig 6-25(d) and 6-26(d). In addition, as discussed earlier, for such a microfluidic system with the substrate thickness equal or larger than 1mm, the

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resistance to the heat conduction in the substrate is comparable with that to the heat convection between substrate surface and the surrounding air, hence the resistance to the heat conduction in the substrate is not negligible as compared with the overall resistance (a sum of the resistance to the conduction and to the convection). Therefore, the temperature gradient exists in both the glass and PDMS substrates, which are shown in Fig 6-25 and 6-26. On the other hand, the contour lines in the PDMS substrate are much denser than those in the glass substrate as shown in both Fig 6-25 and Fig 6-26, which suggests that the temperature gradient in the PDMS substrate is much larger than that in the glass substrate due to the much lower thermal conductivity of PDMS than that of glass substrate.

In addition, taking a close examination to Fig. 6-25c and Fig 6-26c, it can be seen that there is large temperature increment from the inlet channels to the mixing channel near T-section. It is because the electric field strengths in the inlet channels are approximately half of that in the mixing channel, since the area of cross-section for the mixing channel is half of that for the inlet channels (sum of inlet channel 1 and inlet channel 2). Thus, heat generation due to Joule heating in the mixing channels is nearly double of that in the inlet channels.

Further comparing the temperature distributions in Fig 6-25 with those in Fig 6-26, it can be observed that with an increase in the Joule number, the temperature of the chip system increases significantly. This is because the Joule number combines the parameters affecting on Joule heating generation, such as electric field strength, electrolyte concentration, etc.

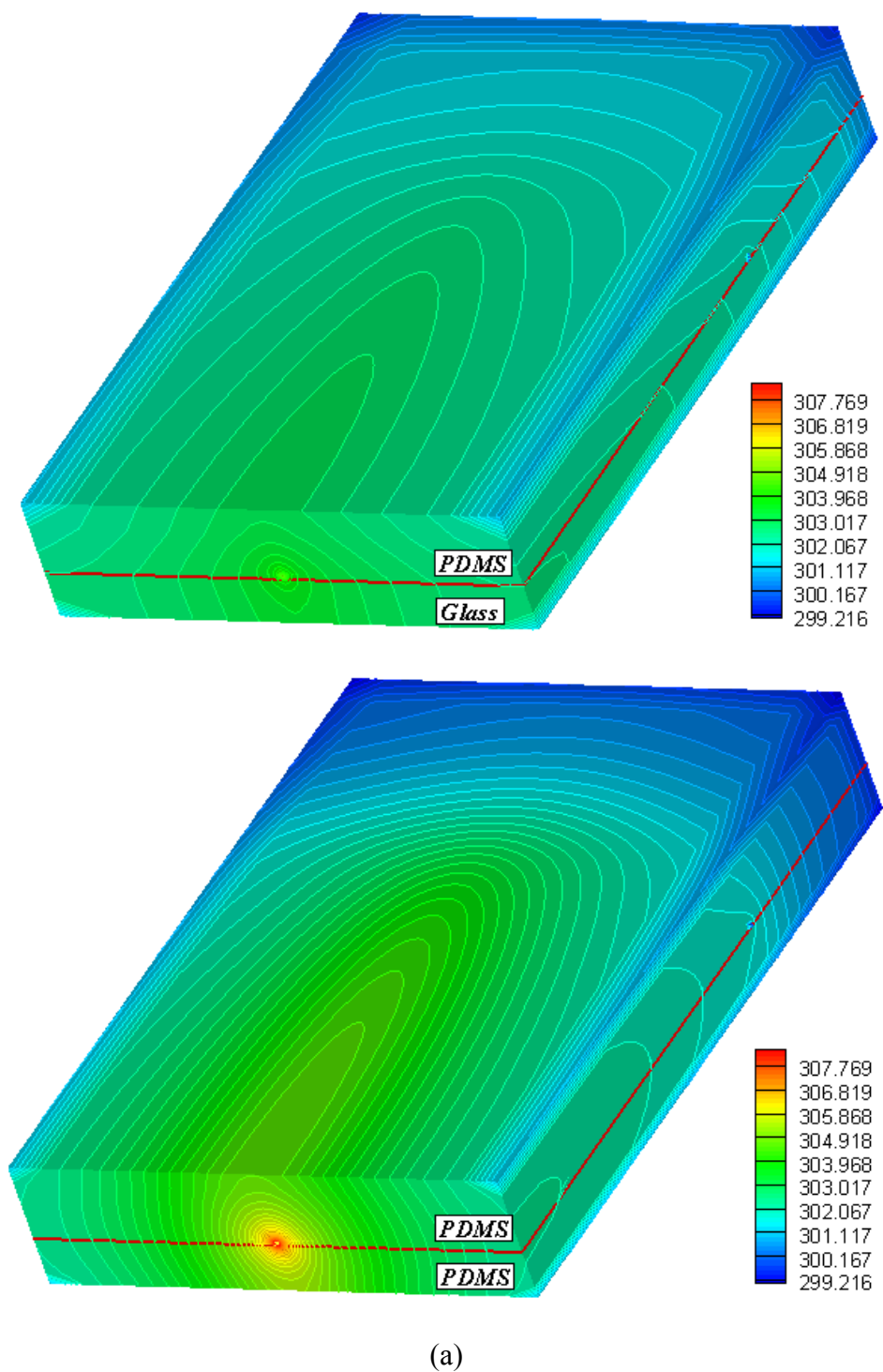
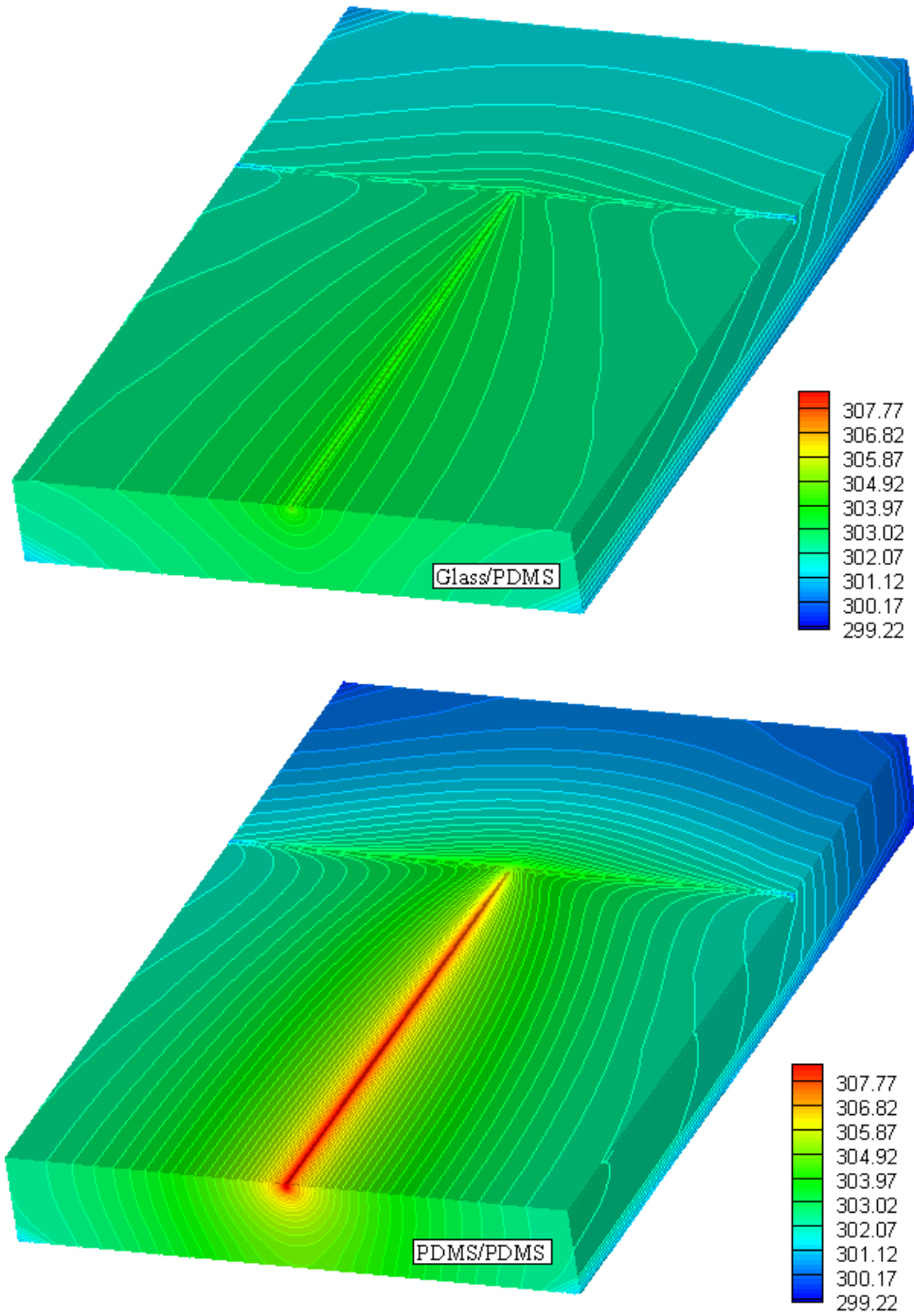


Fig. 6-25 Comparison of the temperature distributions between the PDMS/ PDMS chip system and the Glass/PDMS hybrid system with $Jo = 0.089$ for (a) the temperature contour of the system surface.



(b)

Fig. 6-25 Comparison of the temperature distributions between the PDMS/ PDMS chip system and the Glass/PDMS hybrid system with $Jo = 0.089$ for (b) the temperature distributions around the T-shape channel in the substrate.

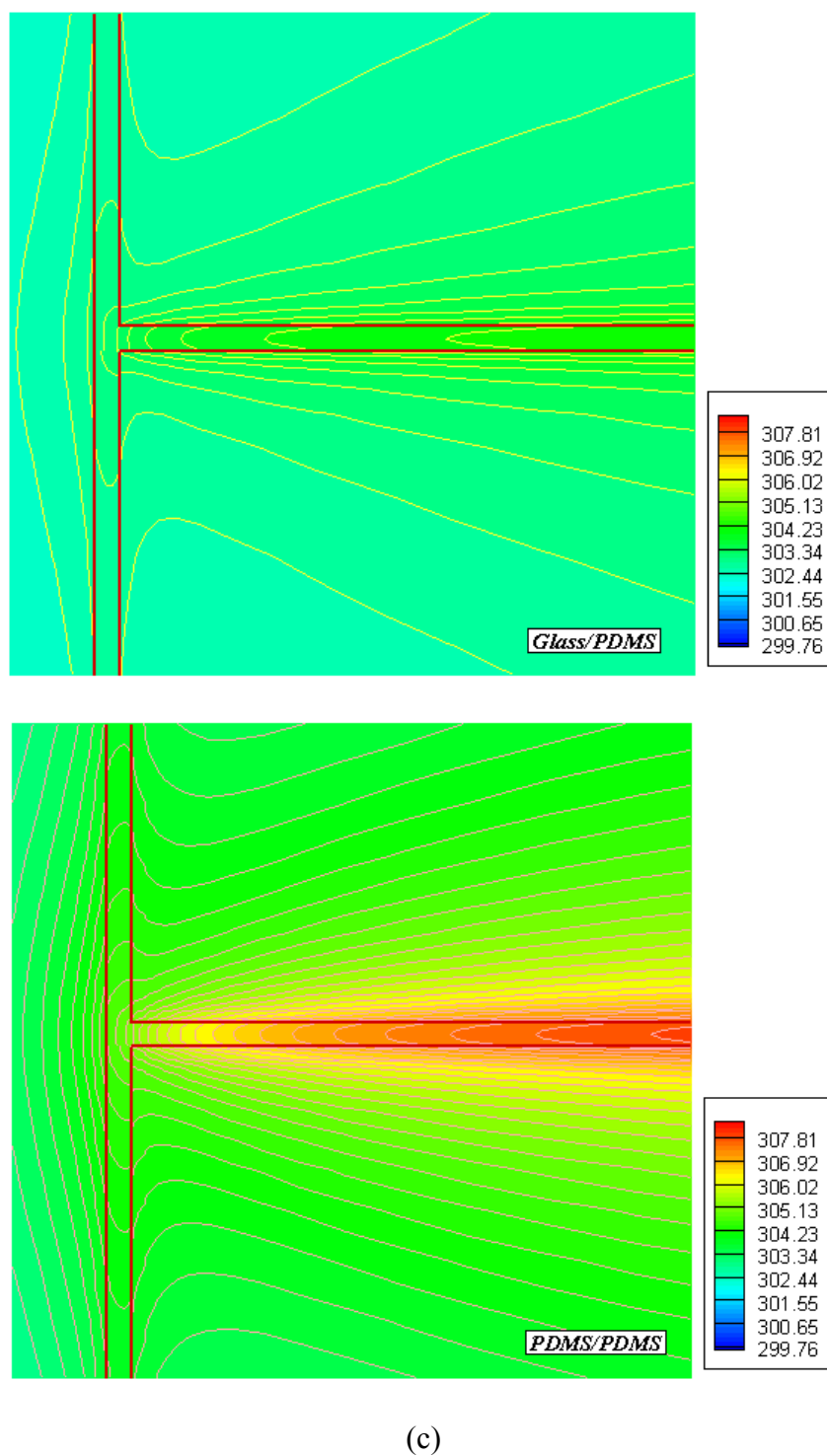
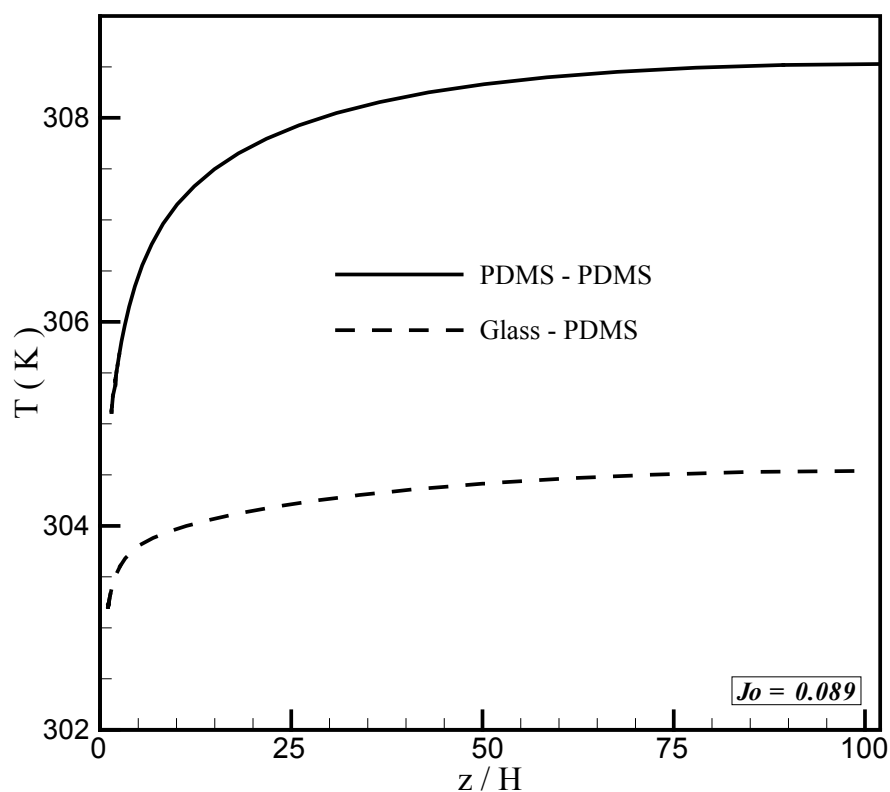


Fig. 6-25 Comparison of the temperature distributions between the PDMS/ PDMS chip system and the Glass/PDMS hybrid system with $Jo = 0.089$ for (c) the detailed temperature contour near the T-section on the T channel plane (i.e. y-z plane).



(d)

Fig. 6-25 Comparison of the temperature distributions between the PDMS/ PDMS chip system and the Glass/PDMS hybrid system with $Jo = 0.089$ for (d) variation of the solution temperature at the centerline of the mixing channel along the flow direction.

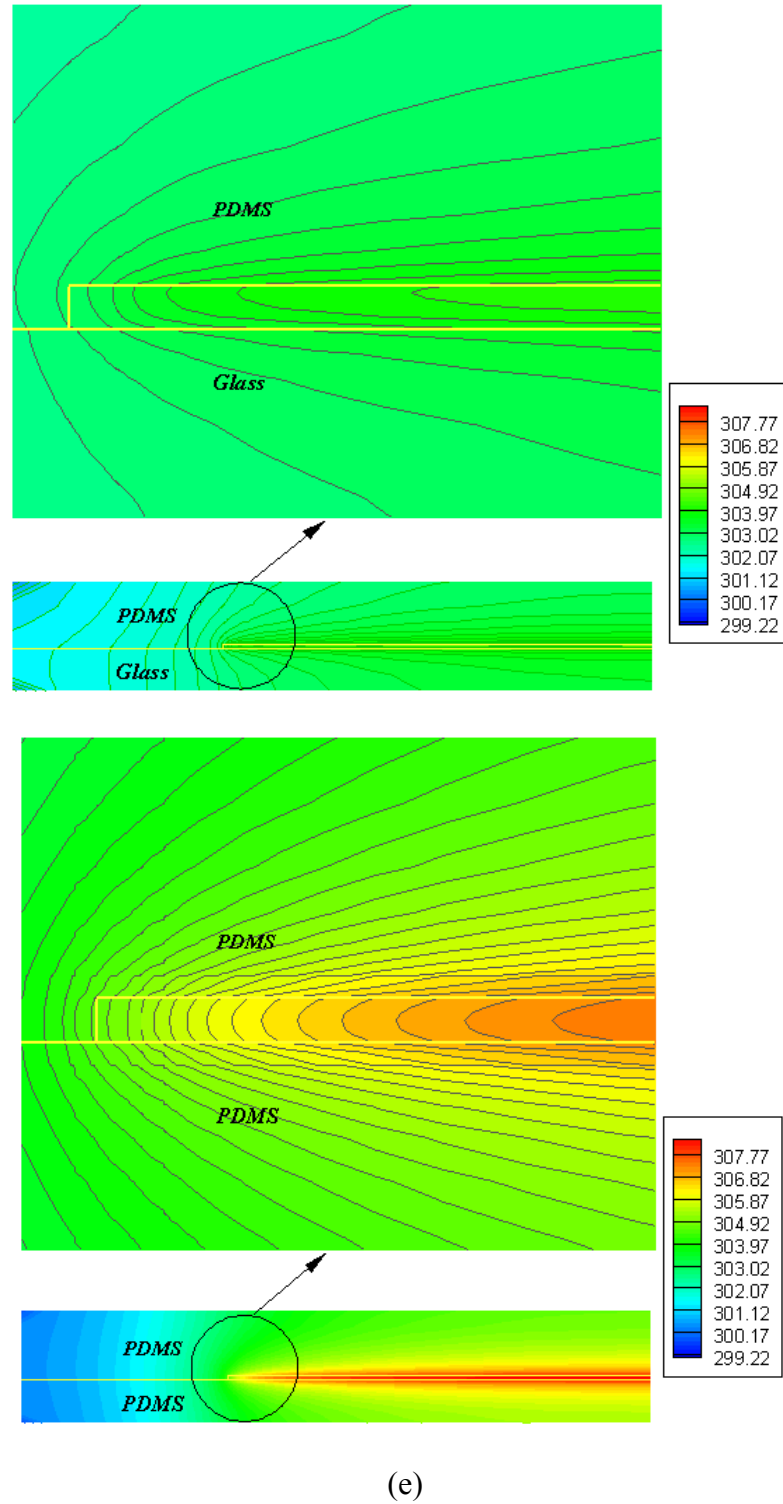
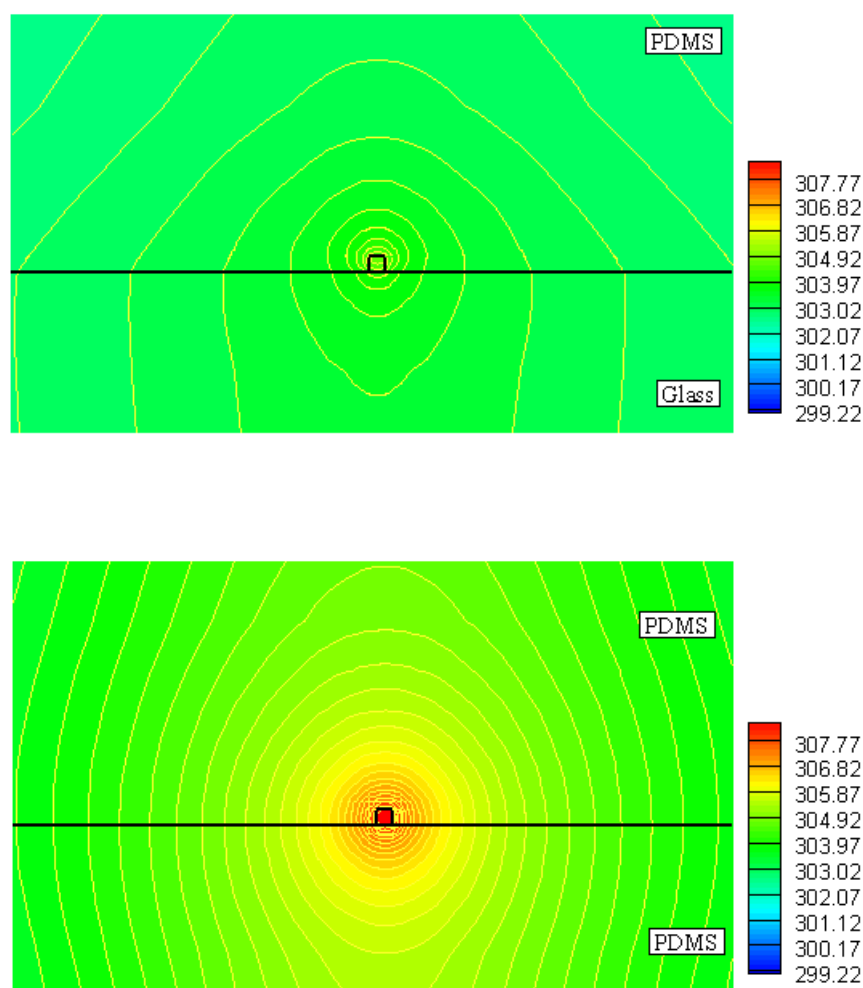


Fig. 6-25 Comparison of the temperature distributions between the PDMS/ PDMS chip system and the Glass/PDMS hybrid system with $Jo = 0.089$ for (e) the detailed temperature distributions near the T section on the plane perpendicular to the T-channel (i.e., x-z plane)



(f)

Fig. 6-25 Comparison of the temperature distributions between the PDMS/ PDMS chip system and the Glass/PDMS hybrid system with $Jo = 0.089$ for (f) the temperature distributions varying along x, y direction in the thermally developed region.

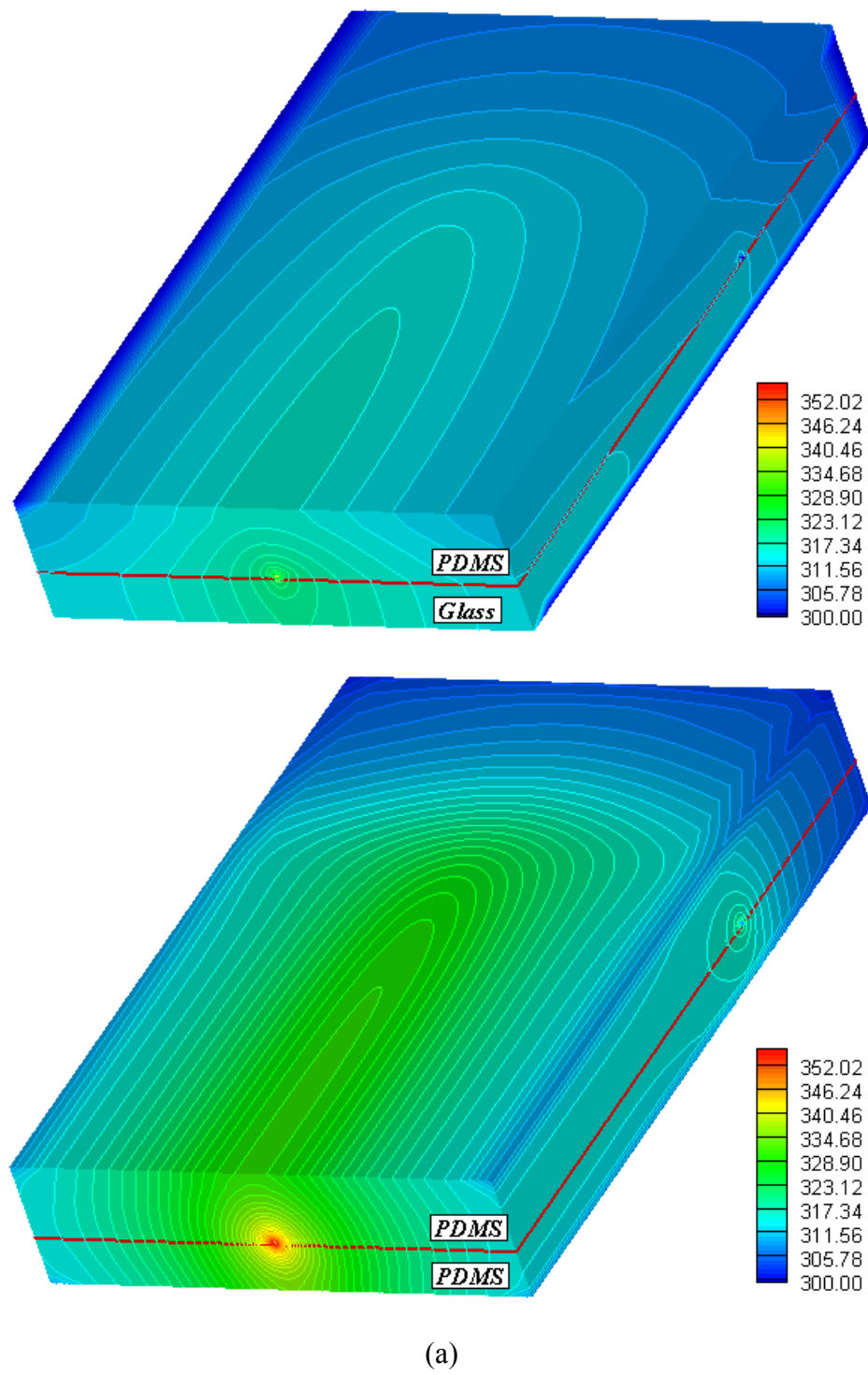
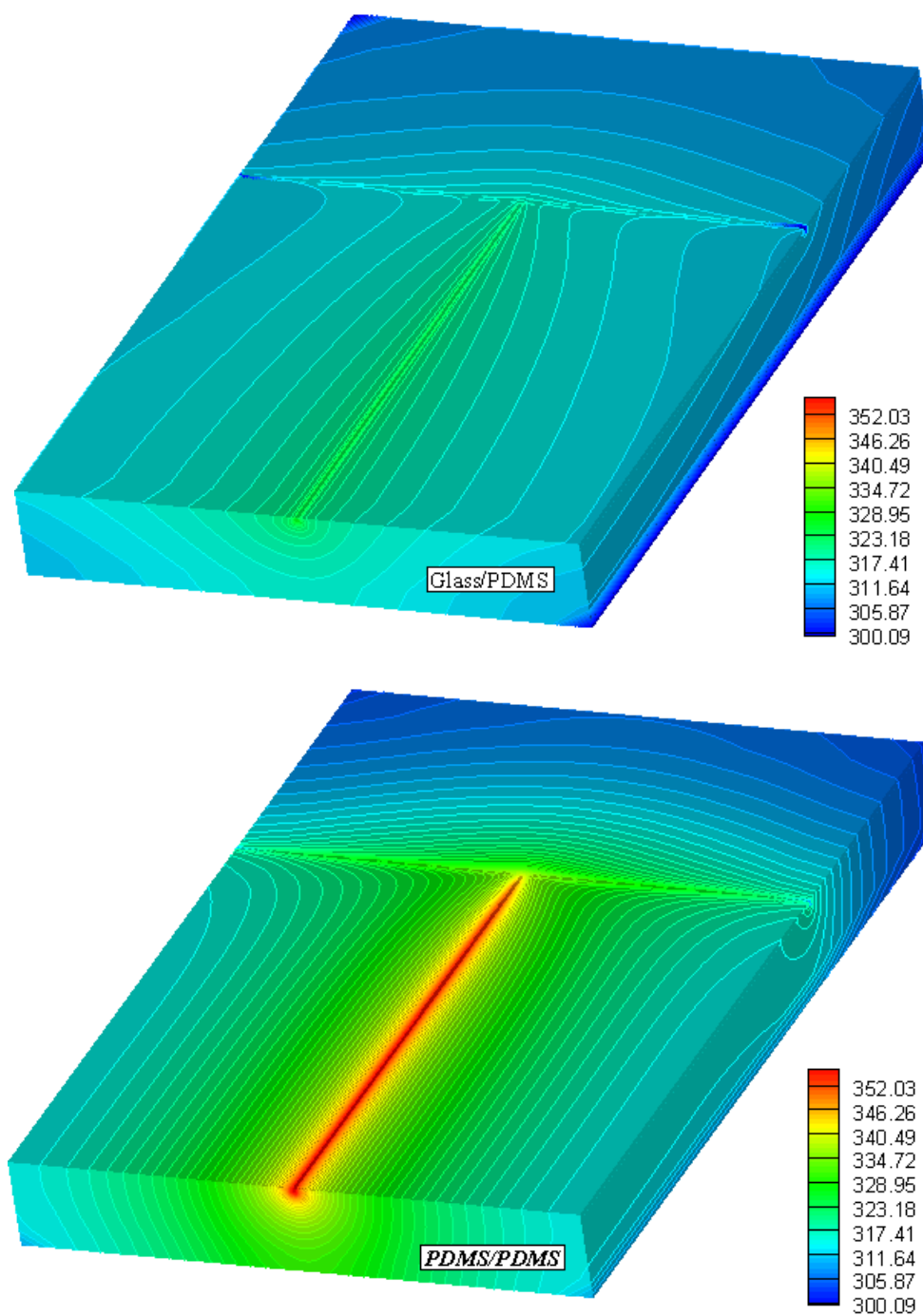
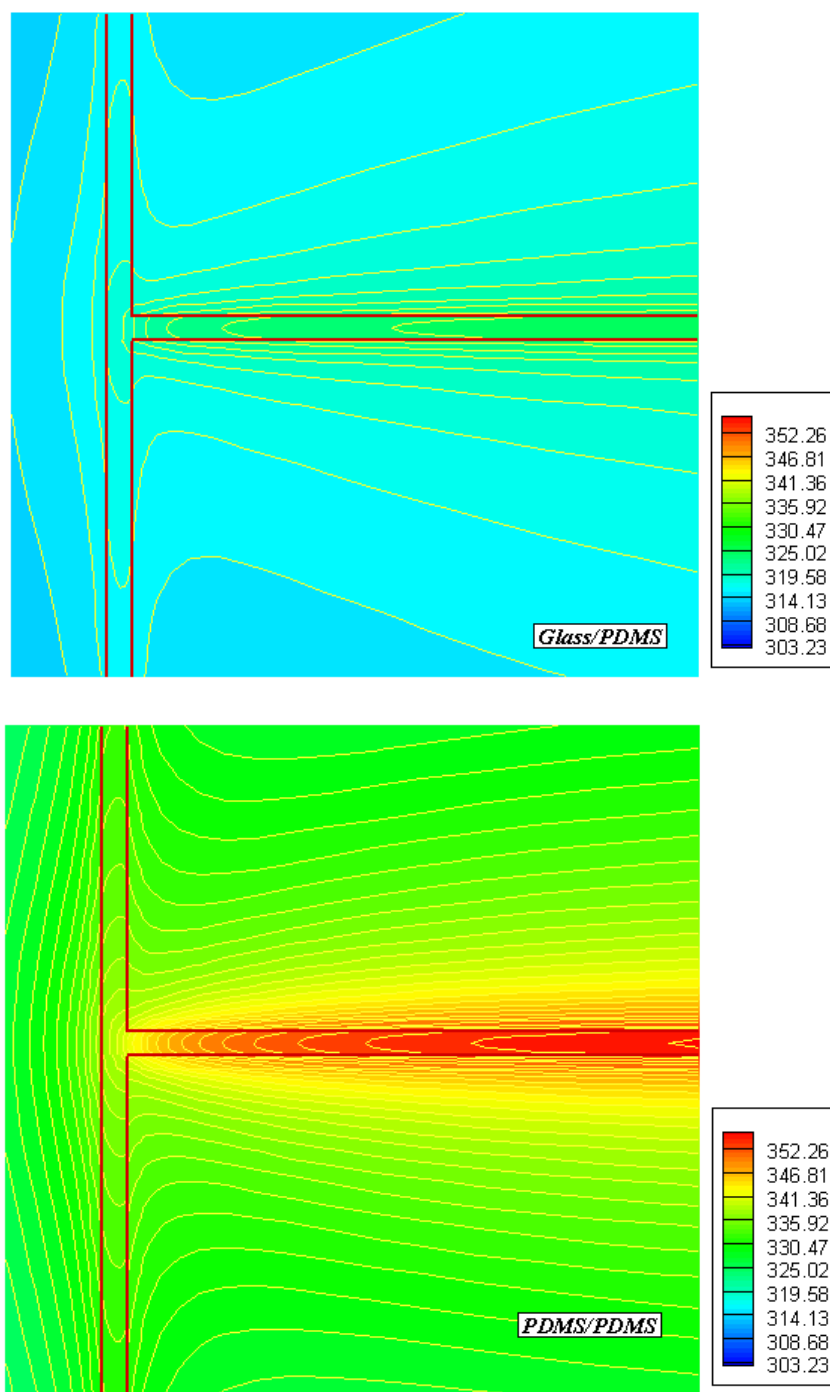


Fig. 6-26 Comparison of the temperature distributions between the PDMS/ PDMS chip system and the Glass/PDMS hybrid system with $Jo = 0.285$ for (a) the temperature contour of the system surface.



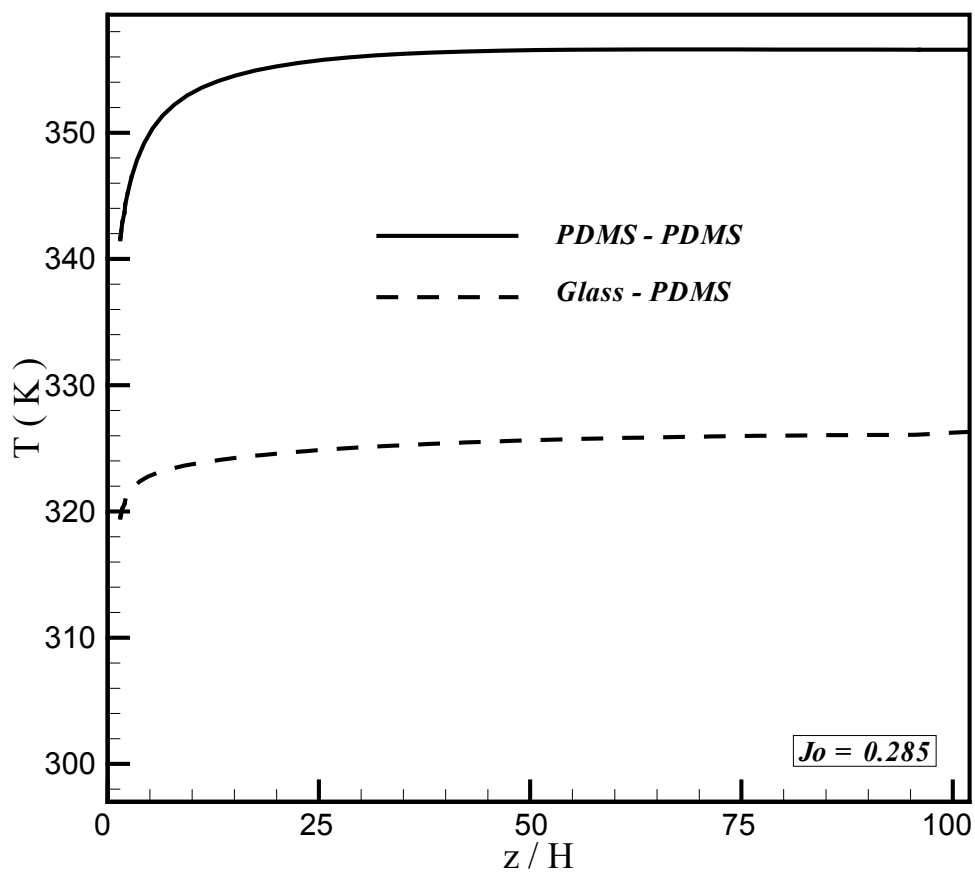
(b)

Fig. 6-26 Comparison of the temperature distributions between the PDMS/ PDMS chip system and the Glass/PDMS hybrid system with $Jo = 0.285$ for (b) the temperature distributions around the T-shape channel in the substrate.



(c)

Fig. 6-26 Comparison of the temperature distributions between the PDMS/ PDMS chip system and the Glass/PDMS hybrid system with $Jo = 0.285$ for (c) the detailed temperature contour near the T-section on the T channel plane (i.e. y-z plane).



(d)

Fig. 6-26 Comparison of the temperature distributions between the PDMS/ PDMS chip system and the Glass/PDMS hybrid system with $Jo = 0.285$ for (d) variation of the solution temperature at the centerline of the mixing channel along the flow direction.

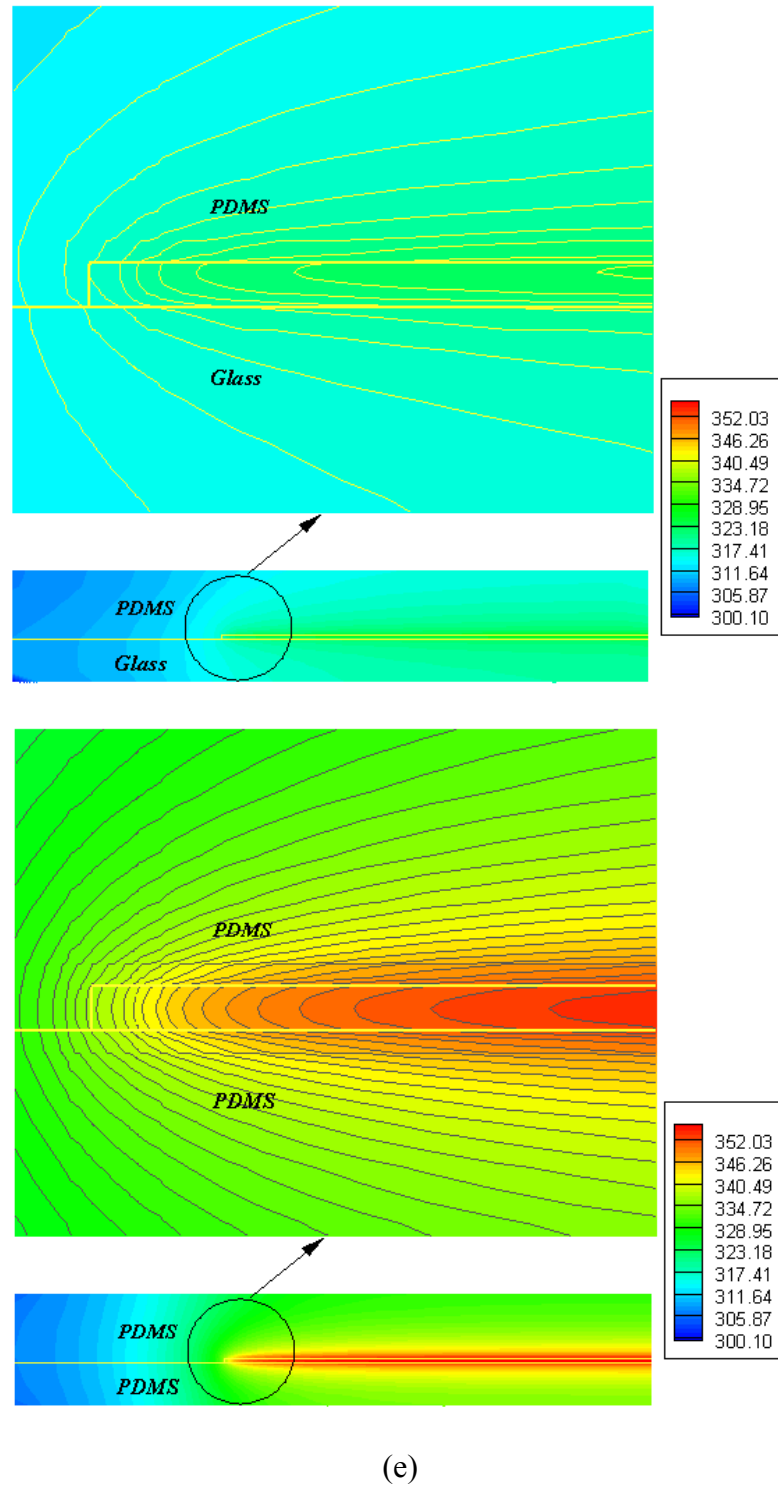
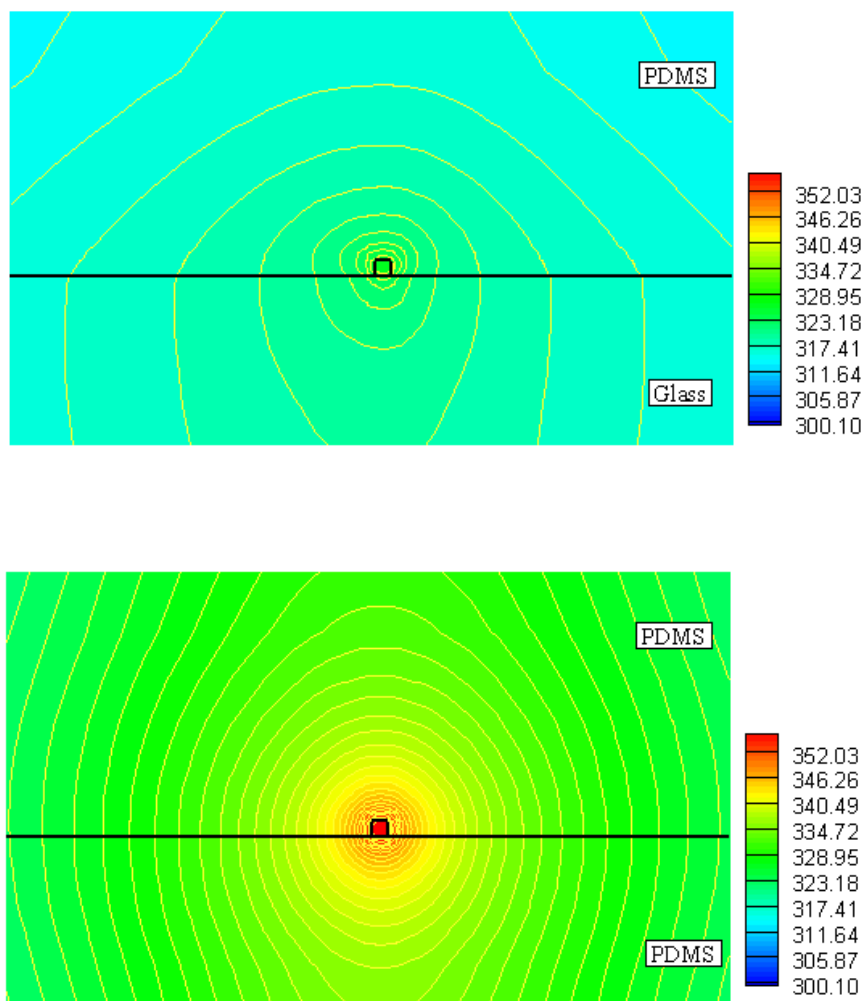


Fig. 6-26 Comparison of the temperature distributions between the PDMS/ PDMS chip system and the Glass/PDMS hybrid system with $Jo = 0.285$ for (e) the detailed temperature distributions near the T section on the plane perpendicular to the T-channel (i.e., x-z plane).



(f)

Fig. 6-26 Comparison of the temperature distributions between the PDMS/ PDMS chip system and the Glass/PDMS hybrid system with $Jo = 0.285$ for (f) the temperature distributions varying along x, y direction in the thermally developed region.

6.4.3 Electroosmotic flow field with Joule heating effects

The electroosmotic flow velocity vectors in the midplane of a PDMS/PDMS chip system and a Glass/PDMS chip system are presented in Fig 6-27 for three different cases: (a) without Joule heating effects, (b) with Joule heating effects ($Jo = 0.089$) and (c) with Joule heating effects ($Jo = 0.285$). It can be seen that, without Joule heating effects, the velocity exhibits flat profiles in most regimes except near the T section. While with Joule heating effects, the temperature increase leads to a decrease of solution viscosity, and hence results in an increase of electroosmotic velocity. Furthermore, it can also be observed in Fig.6-27 that, with the same Joule number, the PDMS/PDMS system can generate larger temperature increment than that of the Glass/PDMS system, and hence leads to larger velocity increment. In addition, a larger Joule number induces higher temperature, and thus gives rise to larger electroosmotic flow velocity.

As pointed out in previous sections, the electroosmotic flow velocity tends to increase with temperature due to its inverse relationship with viscosity. The local velocity profile is determined by a combined electroosmotic flow and induced pressure gradient. Conceptually, for a straight channel, the induced inner pressure gradient is attributed to the change of the viscosity and electric field strength, which are resulted from the variation of solution temperature when Joule heating is present. However, for the T-section channels, the mechanisms inducing the inner pressure gradient are much more complicated than those in the straight channels. For the T-section channels considered in this section, the cross-section area along the flow direction changes, namely, the cross-section areas in the inlet channels are different from that in the mixing channel. On the one hand, such difference itself can induce the inner pressure gradient; on the other hand, it can also lead to the variation of applied electrical field strength along the flow direction,

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further causing larger temperature change between the inlet channels and the mixing channel. And the large temperature change in turn will result in larger electric field variation. In addition, with Joule heating effects, in both the inlet and outlet region far away from the T-section, the velocity profiles no longer remain in their flat shapes. It can be found from Fig. 6-27 that the velocity profiles exhibit convex shapes at the inlet regions and concave shapes at the outlet regions, and the distortions of the velocity profiles from its flat shapes become more significant with the higher Joule heating induced solution temperature due to the larger Joule number in the PDMS/PDMS microchannels.

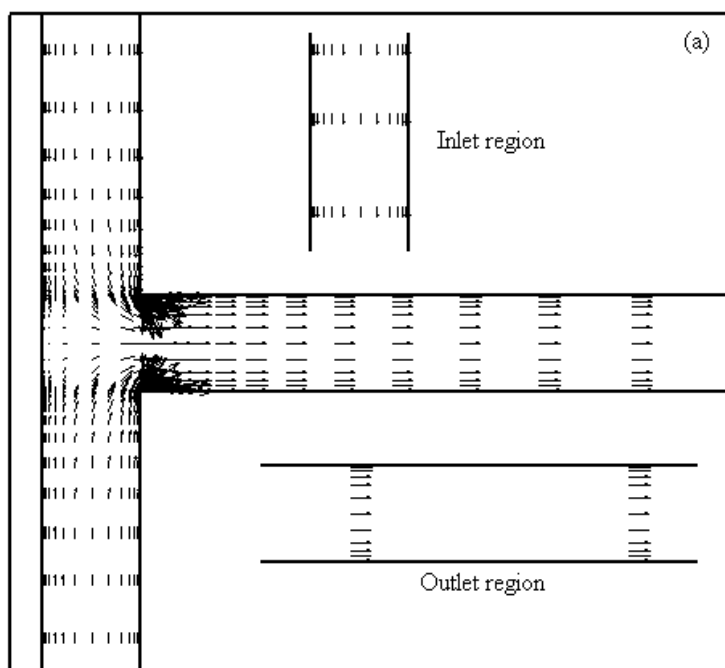


Fig. 6-27 The electroosmotic flow velocity vectors in the midplane of a PDMS/PDMS chip system and a Glass/PDMS chip system for (a) without Joule heating effects.

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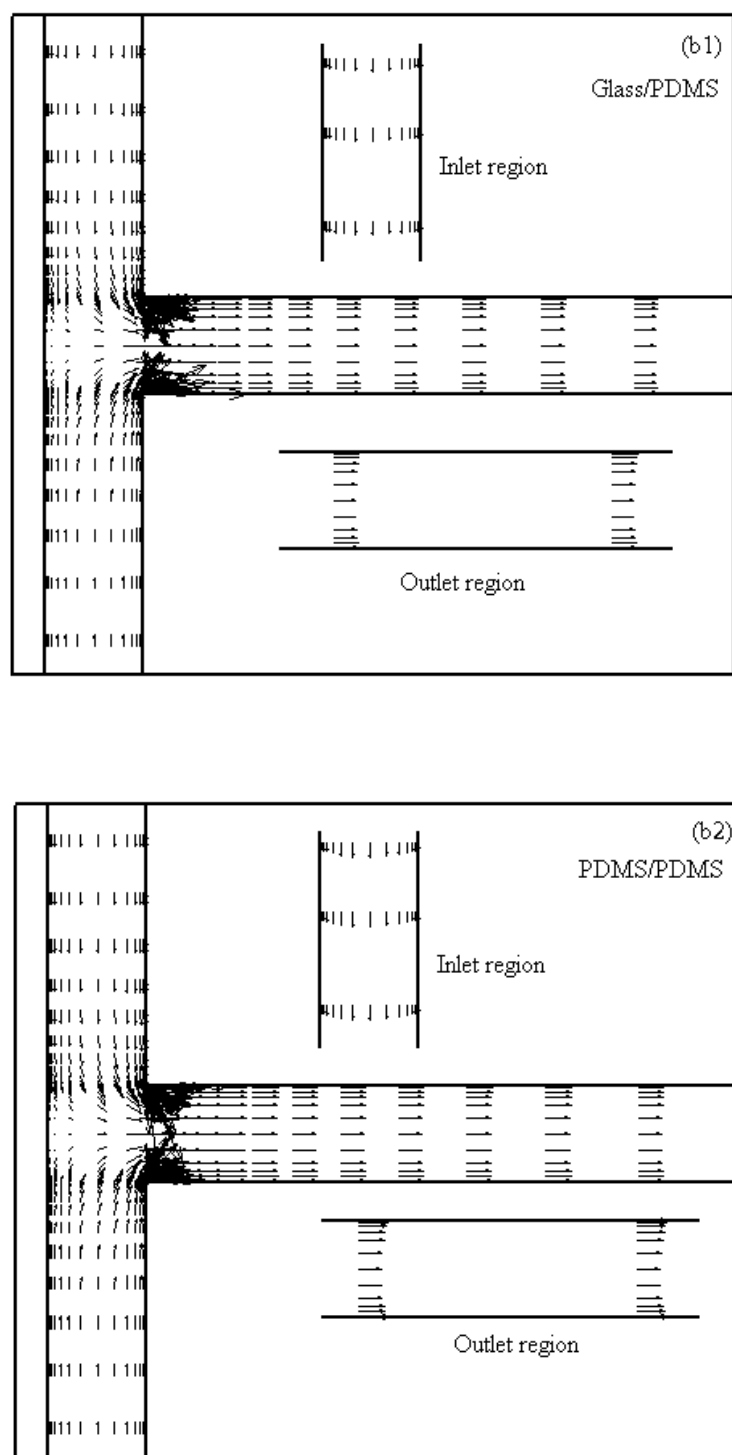


Fig. 6-27 The electroosmotic flow velocity vectors in the midplane of a PDMS/PDMS chip system and a Glass/PDMS chip system for (b) with Joule heating effects ($Jo = 0.089$).

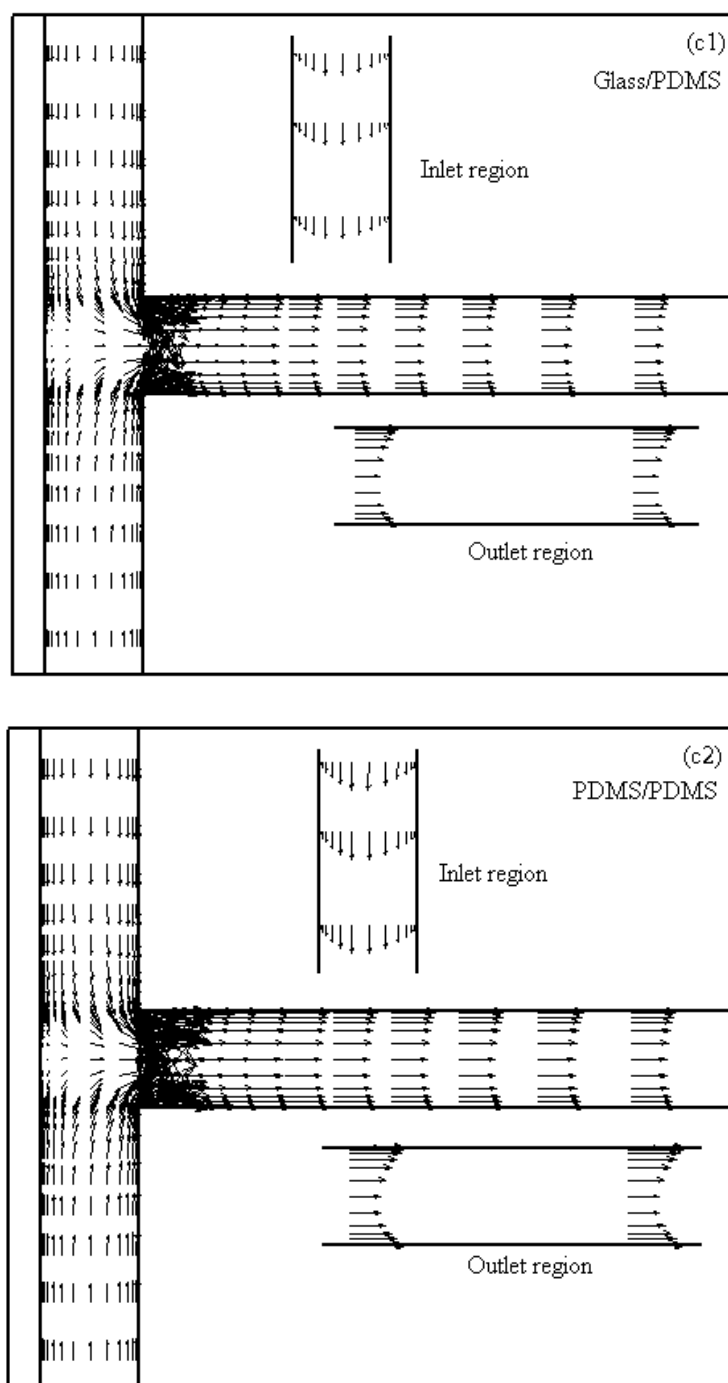


Fig. 6-27 The electroosmotic flow velocity vectors in the midplane of a PDMS/PDMS chip system and a Glass/PDMS chip system for (c) with Joule heating effects ($Jo = 0.285$).

6.4.4 Electrokinetic mixing of sample species in T-shape channels with Joule heating effects

The Joule heating effects on the sample species mixing in T-shape channels are studied in this section. Fig 6-28 presents the 3D concentration distributions in the mixing system, and Fig. 6-29 presents the concentration distributions at the channel midplane for (a) without Joule heating effects and (b) with Joule heating effects (Glass/PDMS system, Joule number is 0.285). The sections 1, 2 and 3 marked in Fig 6-29 locate at the positions of the distance of $400\mu m$, 1.4 mm and 2.4 mm downstream from the intersection. It can be seen that the two streams of sample species from inlet channels 1 and 2 are mixing in the mixing channel. As expected, the symmetric flow field discussed in previous section has yielded symmetric concentration distributions as shown in fig 6-29. The mixing in the considered system is purely diffusive in nature, since mixing occurs in low Reynolds number electroosmotic flow. The mixing of the sample species is very slow and takes a quite long distance (2.4 mm) downstream from the intersection as shown in Fig 6-29. Further taking a close examination to the sample species concentration contour in Fig 6-29a, it can be observed that the mixing is enhanced with Joule heating effects. This enhancement can be attributed to the Joule heating effects on the temperature dependent sample species diffusivity. This enhancement of the mixing with the Joule heating effects can be also obviously noted from Fig 6-30, which compares the cross sectional concentration profiles at the sections 1, 2 and 3 for (a) without Joule heating effects and (b) with Joule heating effects. It can be seen from Fig.6-30 that the difference of the sample species concentration profiles without/with Joule heating effects is not distinguished at the section 1. While at the section 3, a more uniform sample species distribution can be found in species concentration contour of with

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Joule heating effects. This suggests that there is a stronger mixing with Joule heating effect than that without Joule heating effects.

The quantitative comparison of the sample species concentration profiles with/without Joule heating effects is presented in Fig 6-31, which gives the sample species concentration profiles in the midplane along y direction at sections 1, 2 and 3. It can be clearly seen that with Joule heating effects, the concentration gradient along y direction is smaller than that without Joule heating effects, and the difference increases with the increase of distance downstream from the intersection.

The parameter effect on the sample species mixing is indicted in Fig. 6-32, which presents the sample species concentration profiles in the midplane along y direction at section 3 for different Joule numbers and chip systems described in previous sections. As previously discussed, a larger Joule number causes higher solution temperature and higher diffusivity of the sample species, hence resulting in the enhanced sample mixing by displaying more uniform sample concentrations as shown in Fig 6-32. Meanwhile, the PDMS/PDMS system can also lead to higher solution temperature than that of the Glass/PDMS, and for the same reason, it results in smaller concentration gradients along the y direction and thus a better mixing.

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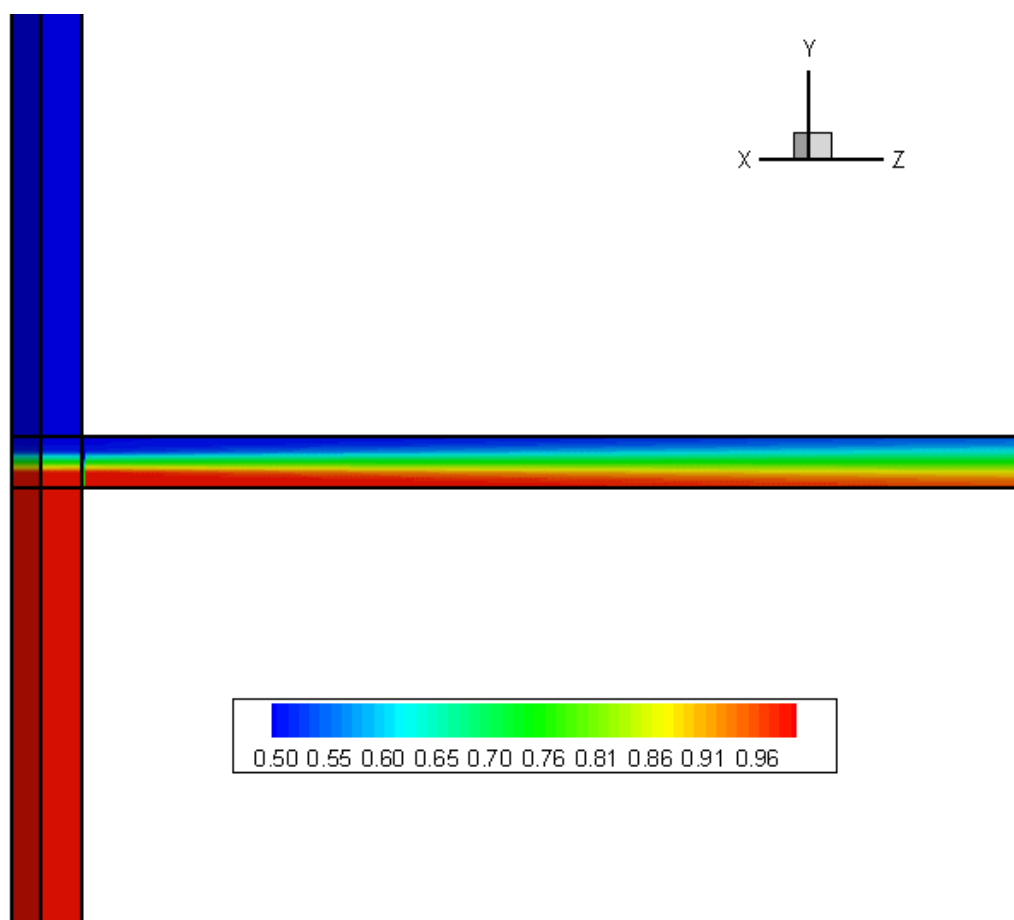


Fig. 6-28 3D sample species concentration contours in the T-shape electrokinetic micro-mixer.

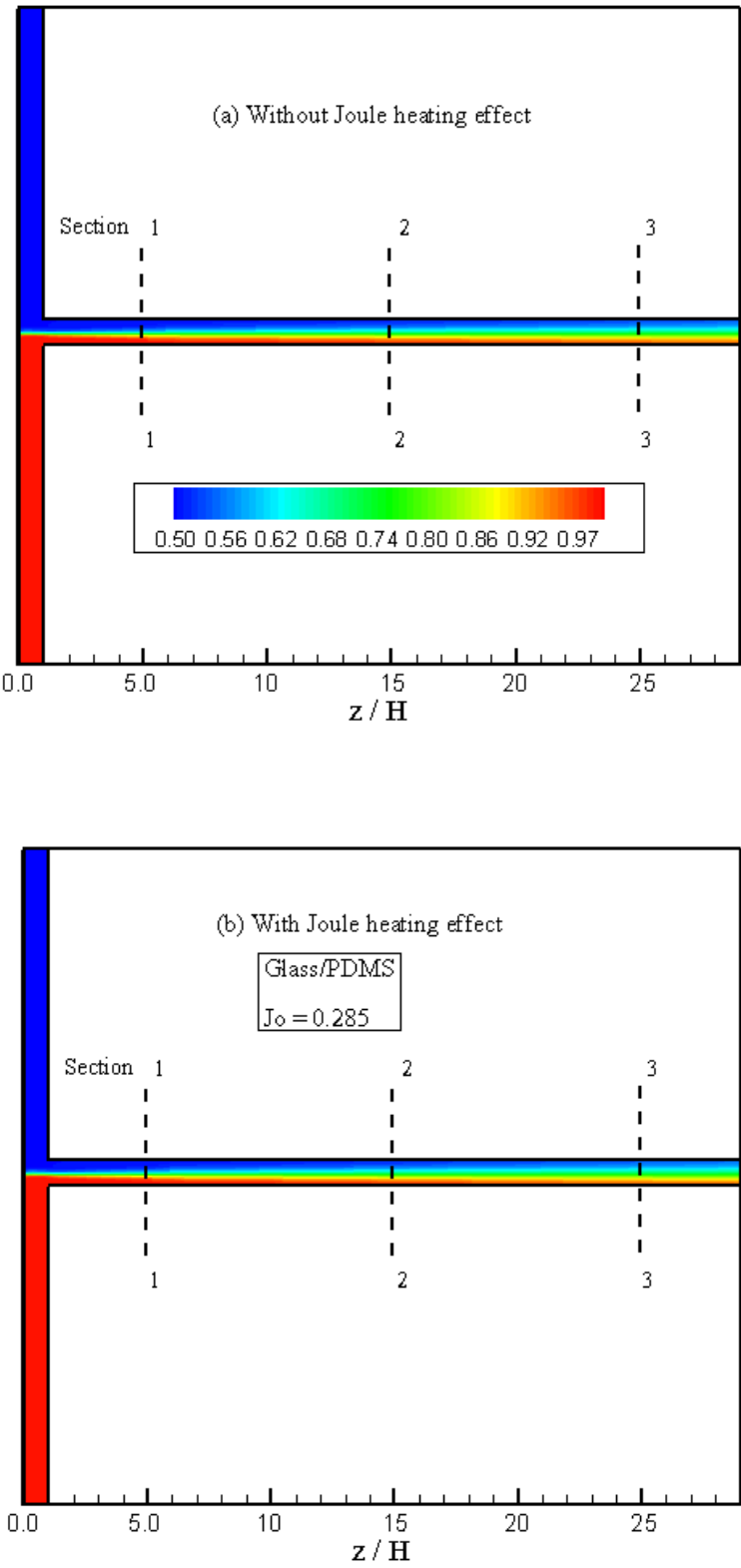
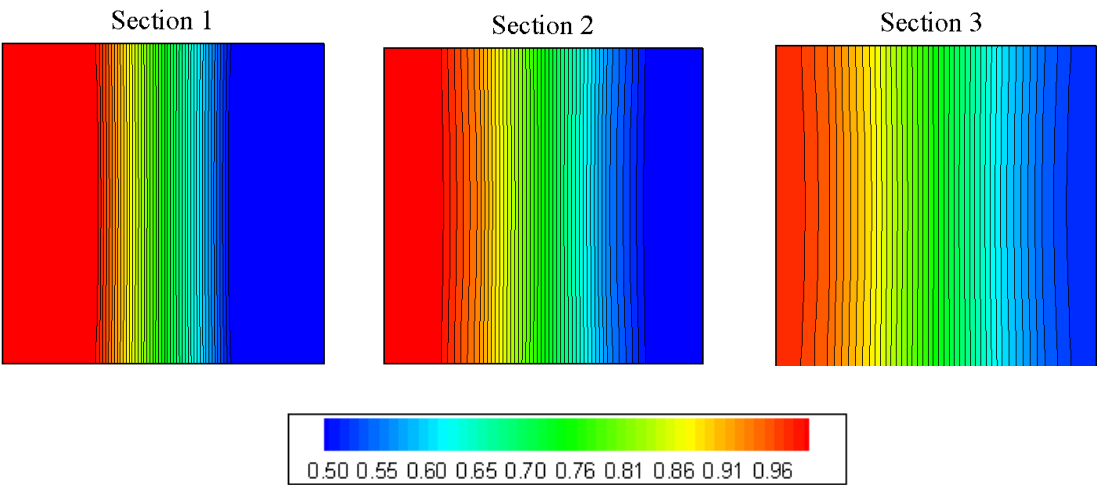
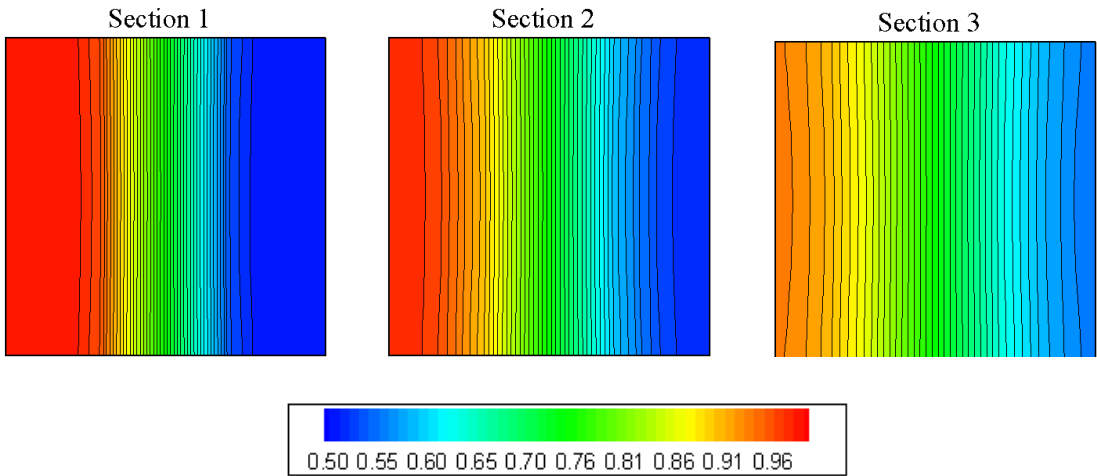


Fig. 6-29 Sample species concentration distributions at the midplane of the T-shape channels for (a) without Joule heating effects and (b) with Joule heating effects



(a)



(b)

Fig. 6-30 Sample species concentration distributions in the cross section of the mixing channel for (a) without Joule heating effects and (b) with Joule heating effects

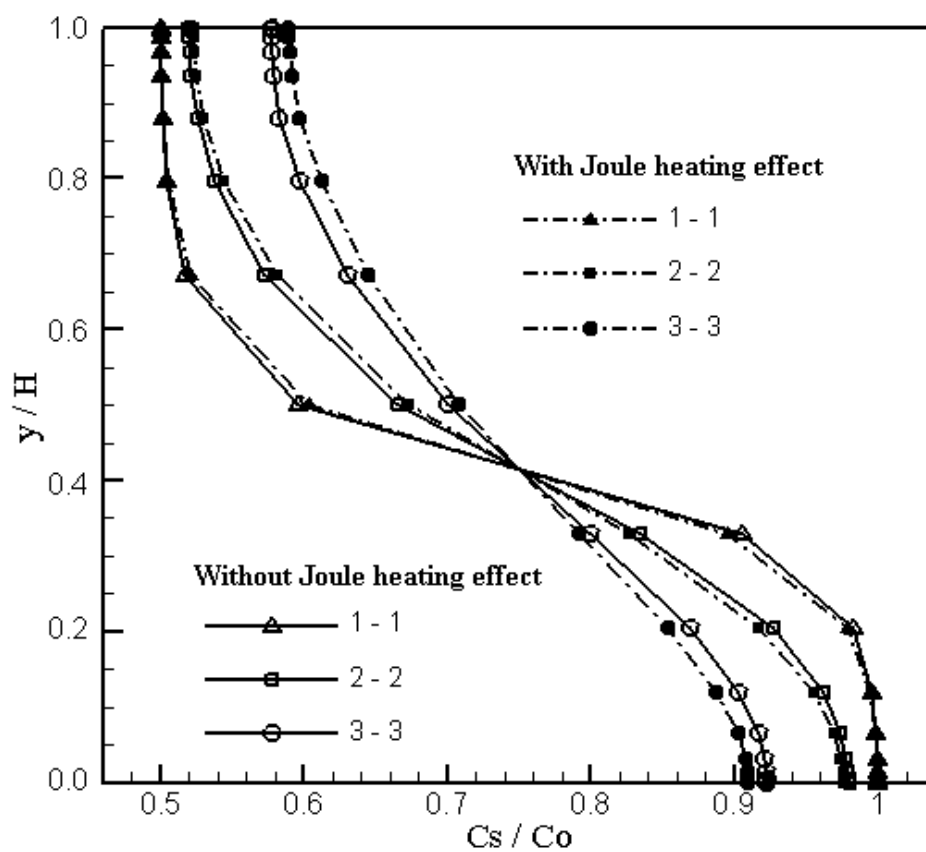


Fig. 6-31 Sample species concentration profiles in the midplane along y direction at sections 1, 2 and 3

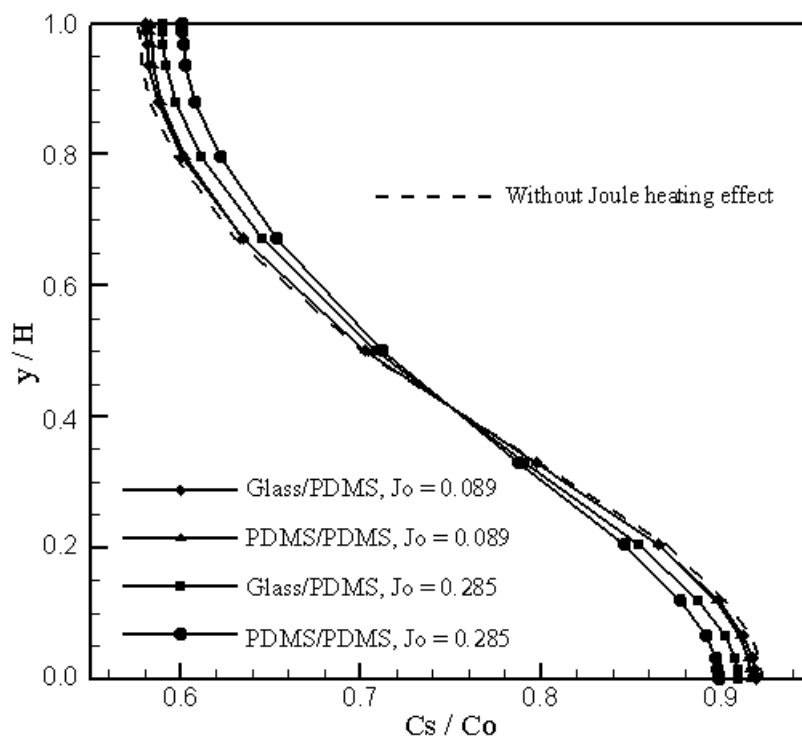


Fig. 6-32 Sample species concentration profiles in the midplane along y direction at sections 3 for different Joule numbers in the PDMS/PDMS and Glass/PDMS systems

6.5 Summary

In this chapter, the 3D coupled mathematical models including the Poisson-Boltzmann equation, Laplace equation, Navier-Stokes equations, conjugate energy equation, and mass transport equation describing the EOF, Joule heating and its effects on the EOF and sample transport in microfluidic systems with rectangular cross section were formulated. The corresponding numerical scheme for solving the proposed 3D models was developed. The numerical simulations of the Joule heating and its effects on in various microfluidic structures including straight channels (both commercial and fabricated using Glass/PDMS and PDMS/PDMS substrates), T-shape

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microchannels fabricated using Glass/PDMS and PDMS/PDMS substrates, and channels with a step change of cross-section fabricated using Glass/PDMS and PDMS/PDMS substrates were carried out.

The simulations showed that due to the low heat transfer coefficient of natural air convection cooling mode, the entrance length of the electroosmotic flow and the Joule heating induced temperature developments in rectangular channels is much larger than that in cylindrical capillaries but with the high heat transfer coefficient of thermostated cooling mode (discussed in chapter 5). Under such a situation, the transverse variation of solution temperature is negligible as compared to the Joule heating induced temperature increment. Furthermore, an unusual heat transfer behavior was observed. When the inner dimension of channels was kept unchanged, it was found that increasing channel wall thickness would result in lower liquid temperatures. Nevertheless, it was concluded that the Joule heating effect is more significant for the system with larger Joule number, thinner wall and poorer thermal conductivity of substrates.

The simulations also showed that the presence of Joule heating effects causes the electroosmotic flow to deviate from its flat profile; the electroosmotic velocity exhibits a concave shape in the developing region and a convex shape in the fully developed region. Correspondingly, the sample band shape for the case of the dispersion of a finite sample plug is distorted.

The simulation for the T-shape channels provided the detailed information and full understanding of the Joule heating induced temperature field and its effects on the electroosmotic velocity field. It was also shown that the Joule heating effect could enhance the electrokinetically driven sample mixing in the T-shape microchannels.

CHAPTER 7

EXPERIMENTAL VERIFICATION OF THE NUMERICAL SIMULATIONS

7.1 Introduction

The importance of fluid temperature control in microfluidic devices has been demonstrated for enzyme-activated reactions (*Tanaka et al.*, 2000), polymerase chain reaction (PCR) amplification of DNA (*Kopp et al.*, 1998), and capillary electrophoresis systems (*Knox and McCormack*, 1994). However, it is a challenging task to measure the fluid temperature in microfluidic channels. Probably the easiest and most straightforward way is to measure the temperature on the outside capillary surface (*Terabe et al.*, 1985) or the substrate of the microchannel (*Lagally et al.*, 2001). But the measured temperature is not accurate as the temperature outside the channel is not necessarily the same as that of the fluid inside the microchannel.

Several techniques have been recently developed for making direct “in-channel” measurements of buffer temperatures in microscale systems, and a critical review was provided by *Ross et al.* (2001). Examples include Nuclear magnetic resonance (NMR) (*Lacey et al.*, 2000), Raman spectroscopy (*Davis et al.*, 2000), and the recently developed on-chip interferometric backscatter detector technique (*Swinney and Bornop*, 2002). The most popular techniques involve the addition of temperature sensitive probes (e.g. thermochromic liquid crystals (*Chaudhari et al.*, 1998), nanocrystals (*Mao et al.*, 2002), or special fluorescent dyes (*Lou et al.*, 1999)) to the buffer solution and an observation of the spatial and temporal changes in the thermal field via some type of microscopy technique. Rhodamine B is a fluorescent dye whose quantum yield is strongly dependent on temperature in the range of 0 °C to 100 °C,

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making it suitable for liquid based systems. Recently *Ross et al.* (2001, 2002) extended a Rhodamine B based thermometry technique developed by *Sakakibara et al.* (1999) for macroscale systems and applied it for monitoring temperature profiles in microfluidic systems.

This Chapter presents experimental study of the Joule heating induced temperature field and its effects on electroosmotic flow. We will make use of a Rhodamine B based thermometry technique to measure the temperature distributions in microchannels. Further, based on the mathematical models developed in this thesis, the numerical simulations predict that the presence of Joule heating has a strong impact on the electroosmotic flow, making it deviate from its normal “plug-like” profile. Thus, the Micro particle image velocimetry (Micro-PIV) technique will be used to measure the profiles of electroosmotic flow under the influence of Joule heating. The experimental results for the Joule heating induced temperature distributions and its effects on the electroosmotic flow field will be compared with the numerical predictions to verify the proposed mathematical models.

7.2 Design and fabrication of the microchannels

The experiments were carried out in both the straight and the T-shape microchannels as shown in Fig. 7-1.

7.2.1 Fabrication techniques

The microchannels used in the experiments were manufactured by using rapid prototyping techniques, which include the photolithography technique for master fabrication and Soft Lithography technique for PDMS microchannels replication. Fig. 7-2 outlines the rapid fabrication of microchannels in PDMS.

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Photolithography is the key technology in MEMS fabrication. Photolithography is the process of transferring geometric shapes on a mask to the surface of a material coated with photoresist, and it involves three sequential steps, as described below.

- Deposition of photoresist film onto the wafer by spin-coating;
- Optical exposure to print an image of the mask onto the resist;
- Immersion in an aqueous developer solution to dissolve the exposed resist and render visible the latent image.

Normally, two types of photoresists are available, namely, the positive and the negative types. For positive resists, the underlying material that is to be removed will be exposed to UV light. For these resists, exposure to the UV light changes the chemical structure of the resist hence, enabling it to become more soluble in the developer. The exposed resist is then washed away by the developer solution, leaving windows of the bare underlying material. The mask, therefore, contains an exact copy of the pattern that is to remain on the wafer. Negative resists behave in the opposite manner. Portions that are exposed to the UV light will result in polymerization of the photoresist, and hence these regions are more difficult to dissolve. Therefore, when immersed in the developer solution only the unexposed portions are removed and the negative resist remains on the surface wherever it is exposed. Masks used for negative photoresists, therefore, contain the inverse of the pattern that is to be transferred.

Soft Lithography, which represents an alternative set of techniques for fabricating micro- and nanostructures, is a microfabrication process on which a soft polymer, such as poly(dimethylsiloxane) or other elastomers, is casted on a mold that contains a microfabricated relief or engraved pattern. That is, the elastomeric stamp is prepared by cast molding: whereby the pre-polymer of the elastomer is poured over the master having a relief structure on its surface, and then is cured and peeled off.

7.2.2 Fabrication of the microchannels

7.2.2.1 Design of mask

The mask design is based on the concept and design of the microchannels used in the experiments. In this work, two kinds of mask patterns (i.e. the straight channel and the T shape channel as shown in Fig. 7-3) were first designed using the AutoCAD software, and then the CAD files were printed on a flexible transparency by using a commercial high-resolution printer.

7.2.2.2 Fabrication of the master

The master is fabricated by using the photolithography techniques. The basic sequence of steps that comprise a complete process fabricating the master is as following:

A. *Glass slides cleaning*

To clean the glass slide, the glass slides were immersed in a mixture of Sulphuric Acid (96% concentration; Ashland, Italy) and Hydrogen Peroxide (30% concentration; J.T. Baker, USA) (7:3, piranha etch) at 120 °C for 20 minutes. After that, the glass slides were cooled down in the air and followed by rinsing with deionised water (DI water) and blown dried by nitrogen gas.

B. *Spin Coating*

A glass slide was held in place by vacuum in a spin-coater (Spincoater model P6700 series, Special Coating Systems, Inc.), and a prescribed amount of photoresist (SU8, 100 series) was poured onto the glass slide. Then the glass slide with the SU8 was left for approximately 25-30 minutes to allow the bubbles in the SU8 to burst, hence during spinning, the layer of SU8 on glass slide will be more uniform.

For a thickness of 100 micro of the SU8 photoresist, the coated glass slide was firstly spun at the rate of 500rpm for 22s followed by 2000rpm for 80s.

C. Soft Bake

This step is to drive off solvent from the spun-on photoresist, improve adhesion of the photoresist, and relieve stress due to the spinning process.

After the spin coating of the SU8 on the glass slides were performed, the glass slides were pre-treated at 65°C for 10 min and 95°C for 30min using another hotplate (Dataplate® Digital Hot Plate, PMC 732 Series) to evaporate the solvent and densify the film. After the soft bake process, the glass slides were allowed to cool before being exposed to UV light.

D. UV Exposure

After a glass side has been coated with resist and suitably soft-baked, it was aligned to the corresponding mask for UV exposure to create a latent image in the photoresist. The degree of exposure was adjusted by controlling the light intensity and exposure time. In the fabrication process, the glass side was aligned properly on the OAI machine (Optical Associates Inc., Model J500-IR/VIS, Mask Aligner, see Fig. 7-4), with the transparency mask placed above. Then the SU8 coated glass slide was exposed to UV light for 2min and 20sec at 350-400nm. Although SU8 is virtually transparent, it is insensitive to wavelength of light above 400nm and has maximum absorption when wavelength is below 350nm. However, excessive dose below 350nm may, therefore, results in over exposure of the top portion of the resist hence, resulting in an exaggerated profile of the sidewall.

E. Post-exposure baking

Prior to the developing process, a post-exposure baking operation is essential to terminate any reactions of the resist still taking place even after the exposure process. After being exposed to the UV light, the slide was post baked in two stages: first at a temperature of 65°C for 3min followed by 95° for 10min. This is to enhance the

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cross-linking of the exposed portion of the SU8. Once this was done, the slide was left to cooled before being placed in the developer.

F. Developing

The cooled glass slide was then placed in a SU8 developer solution (Microchem, Newton, Massachusetts) for 10mins. As such the SU8 photoresist was selectively dissolved in the aqueous developer solution. That is, the unexposed region of the photoresist was dissolved, leaving behind the shape of the microchannel, which was the positive relief of the photoresist.

G. Rinse and Dry

After development, the mold was rinsed briefly with isopropyl alcohol (IPA), then dried with a gentle stream of nitrogen gas.

7.2.2.3 Fabrication of PDMS microchannels

The PDMS microchannel was fabricated by using the Soft lithography techniques. Soft lithography was first tried by using the method that was discovered by *Duff et al.* (1998). It is a faster, cheaper and less specialized way of fabricating devices. Furthermore, it is also more suitable for biological applications rather than using glass or silicon micromachining.

A. PDMS replica molding of master

Liquid PDMS, was prepared by thoroughly mixing the PDMS pre-polymer (SYLGARD 184 Silicone elastomer kit, Dow Corning, Midland, MI) and the curing agent, in the weight ratio of 10:1. Caution was used to avoid the contact of latex rubber (gloves) and liquid PDMS, as this would inhibit curing (*Erickson, et al.*, 2003). The mixture was then left for about 1 hour to allow the air bubbles in the mixture to burst. Then the mixed liquid PDMS was poured over the master and cured at a temperature of 65°C for 2 hours.

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Then the PDMS replica of the master containing a negative relief of microchannels was peeled away from the master. The angle of the walls of the photoresist to the substrate was close to 90° , therefore the microchannels in the PDMS replica were essentially rectangular as shown in Fig. 7-5, which presents the SEM images of the channels in PDMS created by the polymer against a positive relief of photoresist for (a) T section of the channel and (b) straight channel with part of the reservoir. The roughness in the side wall of the PDMS channels arises from the limited resolution of the transparency used as a mask in photolithography to create the positive relief of photoresist.

B. Oxidizing and Bonding the PDMS replica and flat slab (PDMS or glass slide)

After the PDMS channels were peeled off from the master, the reservoirs were punched through with a 1-hole puncher. To form enclosed microchannels, the PDMS replica containing the microchannel should be irreversibly bonded with a flat slab of PDMS or glass slide. According to *Duffy et al.* (1998), the oxidized PDMS has hydrophilic surface, it is easy to fill the microchannels in their experiments by placing liquid in three of the reservoirs and apply vacuum on the fourth due to the strong bond of the oxidized PDMS. On the other hand, it is difficult to fill the microchannels defined by the hydrophobic, conformal contact between an untreated PDMS replica and flat by vacuum because two pieces of PDMS tended to be pulled apart by the force of suction since the untreated PDMS has a hydrophobic surface.

Chaudhury (1991) also pointed out that the bond between the two pieces of oxidized PDMS was sufficiently strong that the two substrates could not be peeled apart without failure in cohesion of the bulk PDMS.

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During the process of microchannels fabrication, we also checked the hydrophobicity of the PDMS surface by measuring contact angles with FTA 200 instrument. A drop of deionised water was dropped onto both untreated and oxidized surfaces of two pieces of PDMS, and was later analyzed using the FTA software (see Fig. 7-6). The figure demonstrated that the original PDMS (untreated) surface is hydrophobic, while the oxidized PDMS surface is hydrophilic.

In order to obtain strong bond between the substrate and hydrophilic wall surface enclosing the microchannels, the PDMS replica and the flat slabs of PDMS or cleaned glass slides were undergone the Oxygen Plasma process using the RIE machine (TECHNICS, Micro-RIE, Series 900-11) (see Fig. 7-7)

The O₂ plasma process, uses 150W for power, at 84mTorr, gas flow at 10sccm. The specimens then undergo exposure of plasma for 2 min. During our fabrication, it was found that PDMS replica that were just removed from the master and cleaned glass slides, yielded the best bonding between the glass slide and the PDMS channel when subjected to O₂ plasma. After the PDMS was put onto the glass slide or PDMS flat slab, leaving it for about 15min to let the bonding process to complete.

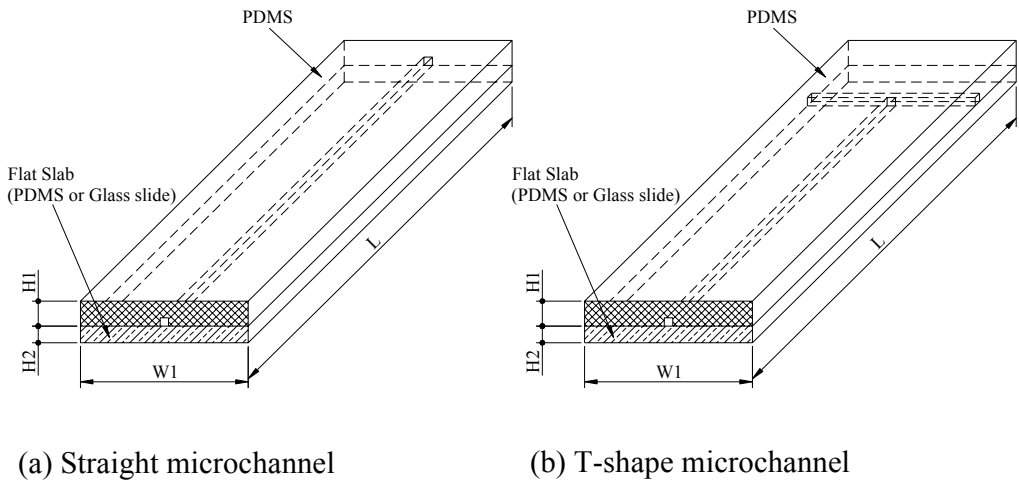


Fig. 7-1 Schematic diagram of the microchannels used in the experiments

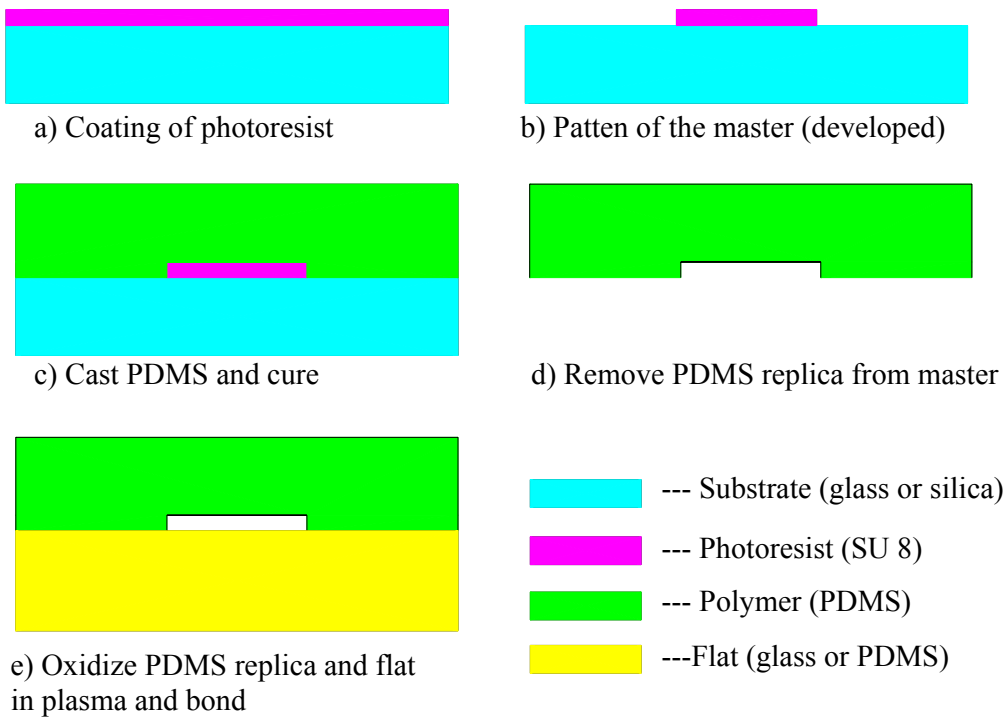


Fig. 7-2 Illustration of the rapid fabrication of microchannels in PDMS

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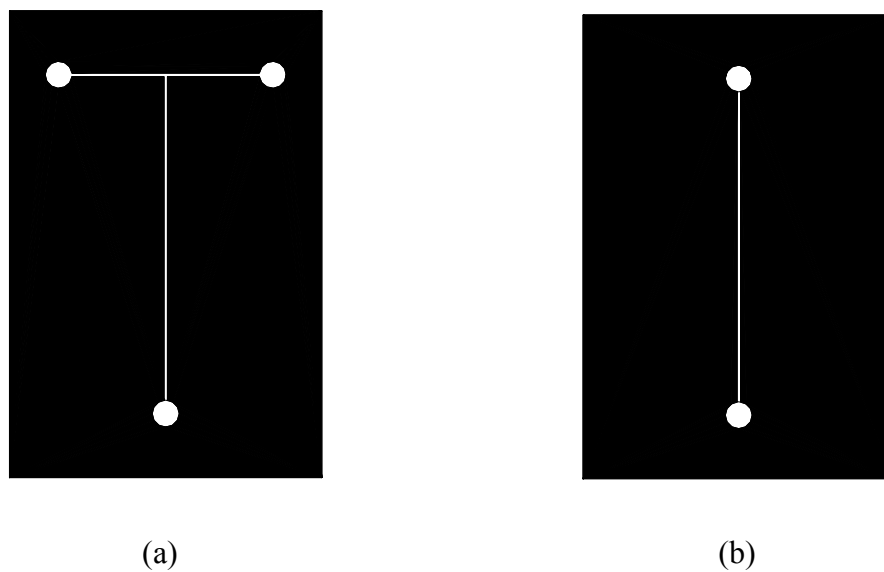


Fig. 7-3 Schematic diagram of the designed masks: (a) T-shape channel, and (b) straight channel

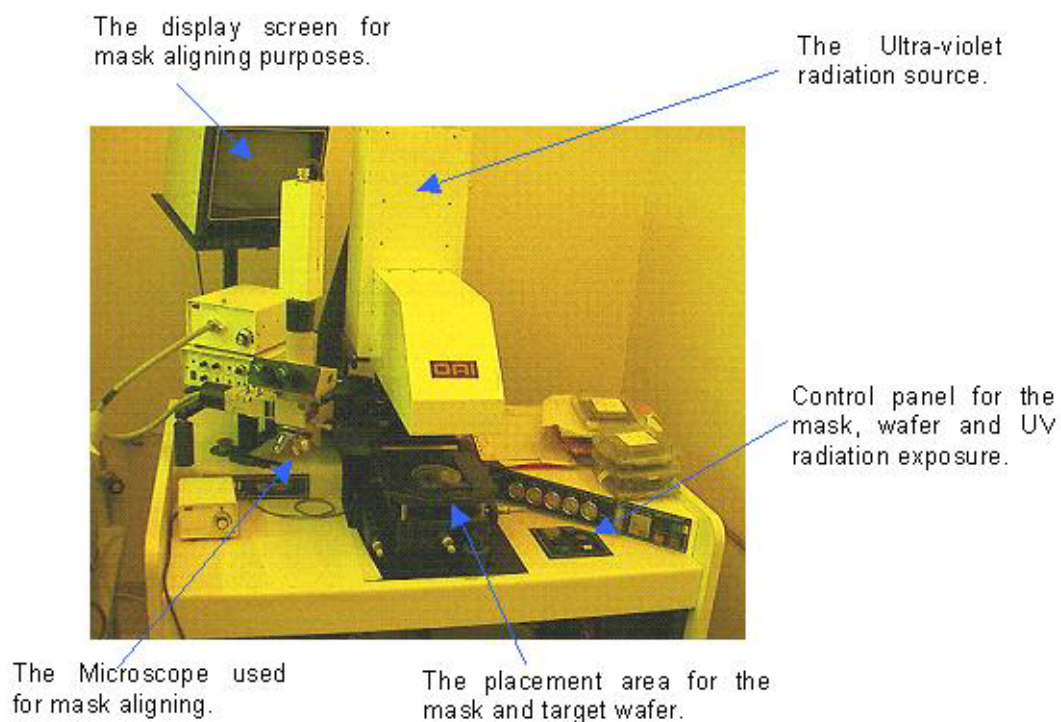
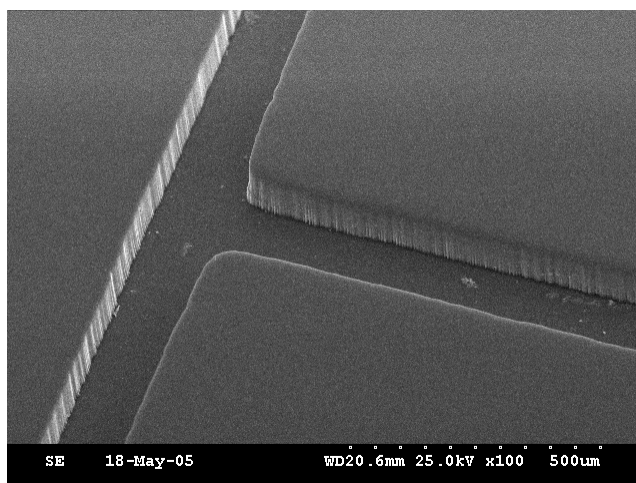
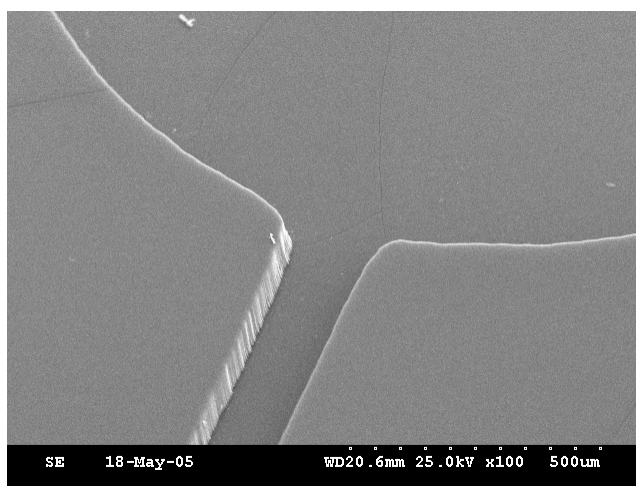


Fig. 7-4 Photo of the exposure machine (Optical Associates Inc., Model J500-IR/VIS, Mask Aligner)

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(a)



(b)

Fig. 7-5 Scanning electron microscopic (SEM) image of the microchannel in PDMS. (a) T-section of the channels (b) straight channel with part of the reservoir

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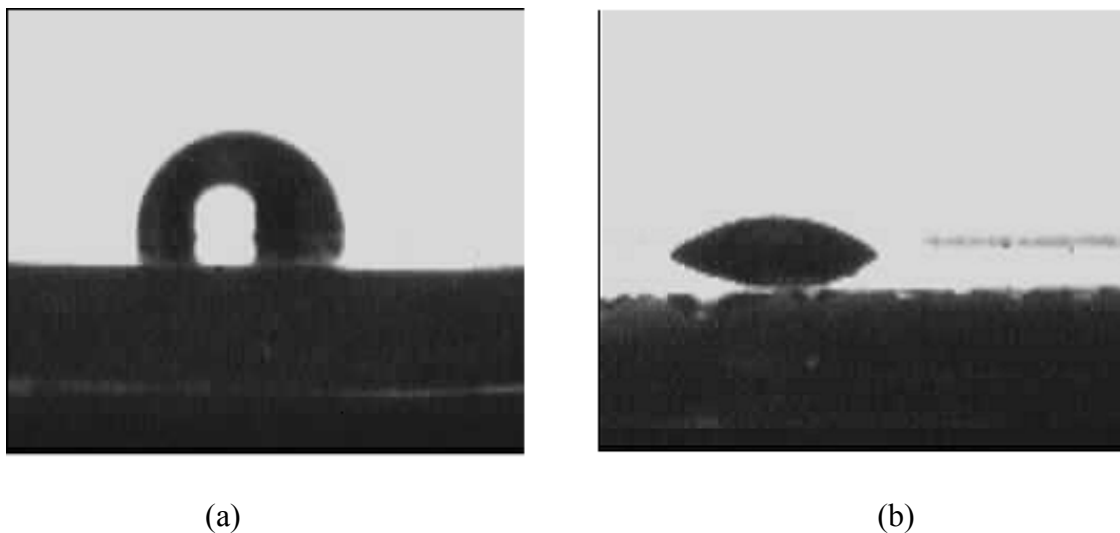


Fig. 7-6 Test for the hydrophobicity of the PDMS surface: (a) before oxygen plasma treatment, and (b) after oxygen plasma treatment



Fig. 7-7 RIE machine used for oxygen plasma etching

7.3 Measurement of the electrolyte temperature distributions in the T-shape microchannels

7.3.1 Experimental technique

A simple technique for the measurement of liquid temperatures in microfluidic structures with good spatial and temporal resolution is employed in this project. The technique takes advantage of the temperature dependence of the fluorescence intensity of a dilute fluorophore added to the working fluid. In brief, the measurement involves comparing the fluorescence intensity at a known, uniform temperature with that at an unknown, possibly nonuniform temperature. The fluorescence intensity is imaged using a standard fluorescence microscope and a CCD camera, so that the spatial resolution is determined by the microscope optics, and the temporal resolution is determined by the rate at which video frames can be captured by the camera. Although this technique requires the addition of a fluorescent dye to the fluid, the high signal-to-noise ratio inherent in fluorescence measurements allows for the use of dilute solutions of dye. Since the fluorescence of many dyes is temperature dependent, a suitable dye can be chosen for each specific application.

Rhodamine B dye is one of a class of fluorescent dyes whose quantum yield is strongly dependent on temperature (*Ross, et al., 2002*). As such the in-channel temperature profile can be obtained by observing the relative spatial and temporal changes in the local intensity of the dye using above-mentioned fluorescence imaging technique.

7.3.2 Chemicals preparation

The working fluid in all cases was an aqueous buffer solution prepared using deionized water (DI water). In the experiments, the Sodium Bicarbonate ($NaHCO_3$) (Sigma, St. Louis, MO) solution was used as the work solution. The concentration of $NaHCO_3$ solution prepared for the experiment was 50mM.

Laser grade rhodamine B dye (Acros Organics, Pittsburgh, Pennsylvania) was initially dissolved in DI water at a concentration of 1 mM and stored at -30 °C. Prior to the experiment the dye was further diluted to a concentration of 0.05mM in 50 mM carbonate buffer solution at a pH of 9.4. All solutions were filtered before use with a 0.2 mm syringe filter (Whatman, Ann Arbor, Michigan).

7.3.3 Direct visualization system for measurement of temperature

Experiments for temperature measurement were conducted using the direct visualization system. A schematic of the experimental setup is given in Fig. 7-8. Experiments were carried out with a fluorescence microscope (Carl Zeiss, Germany) equipped with long-working-distance 5x objectives, a mercury arc lamp and an appropriate filter set (excitation, 546 ± 12 nm, emission, 600 ± 40 nm). A CCD camera (Sensovation AG, Germany) with frame grabbing software (Sensovation SamBa EZ-series IEEE 1394a.) was used to acquire all images. 12-bit, 1024 x 1280 pixel grayscale intensity images were captured every 0.1 s for approximately 90s at an exposure time of 29.85 ms. Pictures captured by the CCD camera were later analyzed by using the Image-Pro® Plus software and finally the temperature distributions were obtained.

7.3.4 Experimental results and discussion

The T-shape microchannel used in the experiment has a length of 5mm for two inlet channels, a length of 20mm for the mixing channel, and a cross-section of $100\mu\text{m} \times 100\mu\text{m}$. In all experiments, a potential of 1050 V was applied to the two inlet reservoirs (# 1 & # 2) and the outlet reservoir (# 3) was grounded. Prior to each experiment the microchannel system was allowed to cool to room temperature and an isothermal “cold field” intensity image of the system was taken. Following the acquisition of the cold field image, the electric field was switched on (inducing electroosmotic flow and joule heating in the microchannel) and full speed image acquisition was initiated and lasted for 90s. Then the electric field was turned off, allowing the system to cool back down to room temperature. After the system cool back to room temperature, a second cold field image was acquired. The second cold field image was then compared to initial image and in general it was found that the intensity values of the two images were identical, suggesting that any photobleaching of the dye during the experiment was not significant. The captured intensity images were then normalized by the cold field image and smoothened by the adaptive filter provided by the software to reduce the effect of any background noise.

The intensity values of treated images were then converted to temperature T using the calibration curve (a third poly-nomial fit) provided by Ross *et al.* (2002), expressed as

$$T = A_0 + A_1 I_n + A_2 I_n^2 + A_3 I_n^3 \quad (7-1)$$

where I_n is the fluorescence intensity normalized by its value at room temperature, and $A_0 = (132 \pm 2)^\circ\text{C}$, $A_1 = (-250 \pm 10)^\circ\text{C}$, $A_2 = (220 \pm 16)^\circ\text{C}$, and $A_3 = (-79 \pm 8)^\circ\text{C}$,

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Fig. 7-9 and Fig. 7-10 present the original images captured by the CCD camera respectively for a PDMS/ PDMS system and a Glass/PDMS system at (a) initial time and (b) thermally steady state (50 s) for the same experimental parameters. It can be directly seen from the figures that at the steady state, that is, 50 seconds after the electric field is applied, the intensity of the Rhodamine B dye in the PDMS/PDMS system is much lower than that in the Glass/PDMS system. This indicates the solution temperature in a PDMS/PDMS system is much higher than that in a Glass/PDMS for the same experimental parameters.

Further converting the intensity value of the Rhodamine B dye to the solution temperature, we can obtain the solution temperature distributions in both the PDMS/PDMS system and the Glass/ PDMS system. Fig. 7-11 presents the experimental temperature contour in (a) PDMS/PDMS system and (b) Glass/PDMS system. The asymmetry in the solution temperature profiles is observed in the two branches before the T-junction. This may be caused by asymmetric structure at the channel/reservoir interface, created during the reservoir cutting process, and/or by asymmetric channel geometry near the T-junction, as a result of the photoresist spin coating process. It can be seen from Fig. 7-11 that as expected the solution temperature in the PDMS/PDMS system is much higher than that in the Glass/PDMS system. It can also be found that the temperature gradient near the T section in the PDMS/PDMS system is larger than that in the Glass/PDMS system.

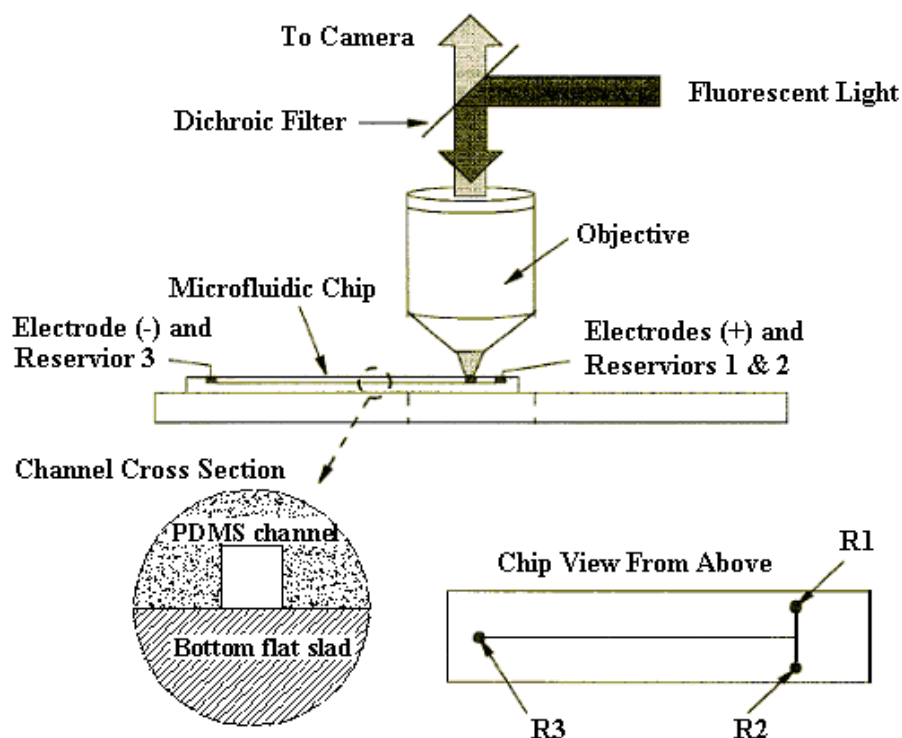


Fig. 7-8 Schematic diagram of the experimental setup for temperature measurements

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(a)



(b)

Fig. 7-9 Images captured by the CCD camera for a PDMS/ PDMS system at (a) initial time and (b) thermally steady state (50 s).

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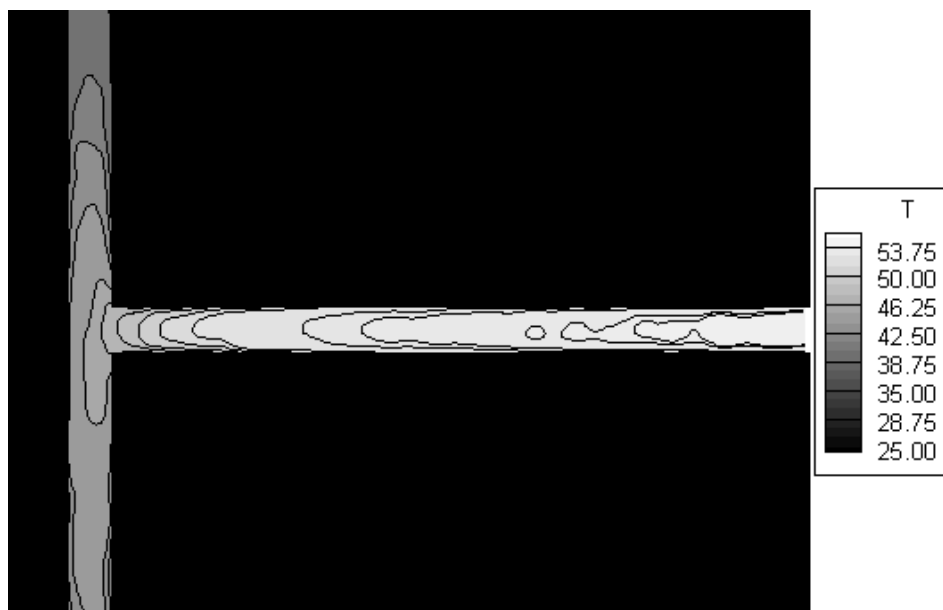
(a)



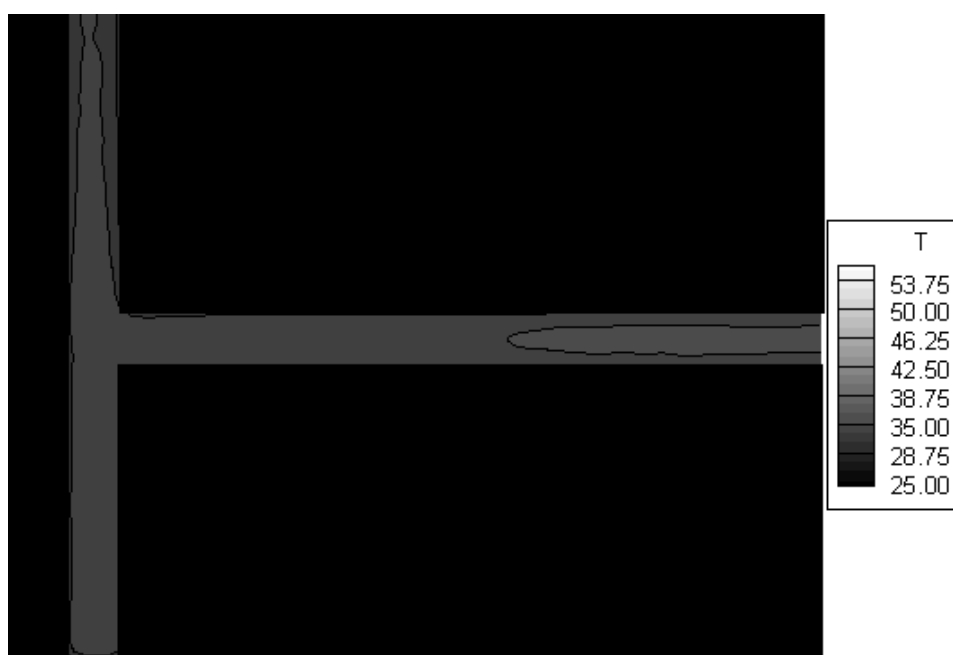
(b)

Fig. 7-10 Images captured by the CCD camera for a Glass/ PDMS system at (a) initial time and (b) thermally steady state (50 s).

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(a)



(b)

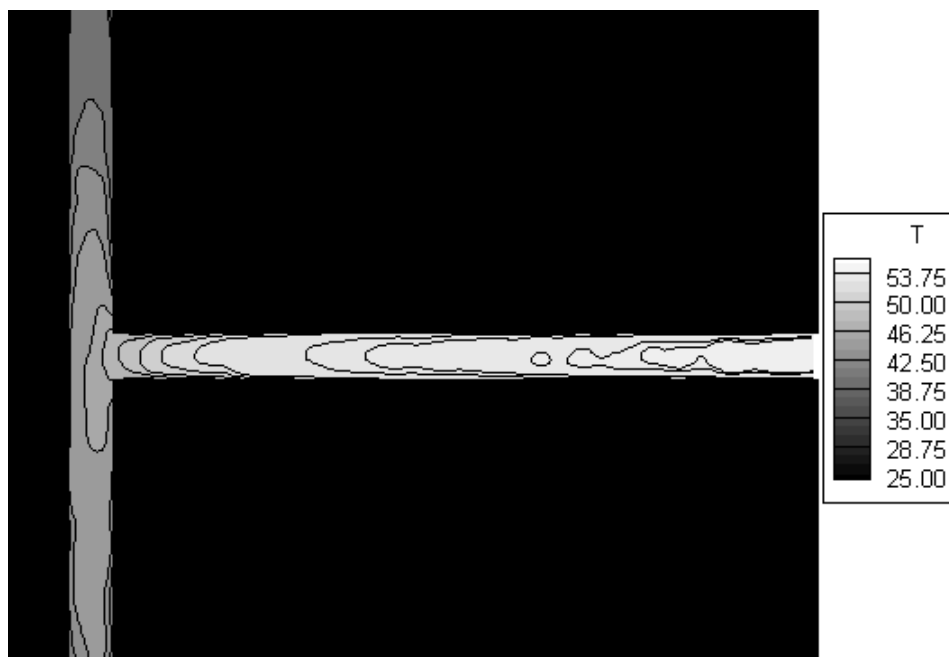
Fig. 7-11 Experimental results of the solution temperature contour in (a) a PDMS/PDMS system and (b) a Glass/PDMS system

7.3.5 Comparison with numerical simulations

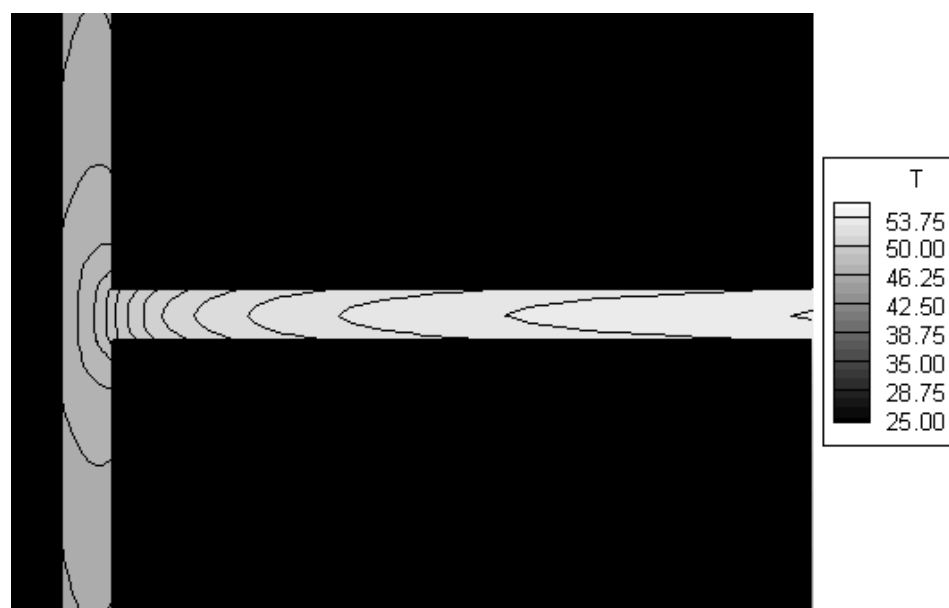
In this section, the experimental results of the Joule heating induced solution temperature distributions are compared with the numerical simulations predicted from the mathematical models developed in this study. The numerical simulations were carried out by using the parameters same as those used in the experiments, including $C = 50mM$, $E_0 = 420V/cm$, and $h = 10W/m^2K$. Fig. 7-12 and Fig. 7-13 present the comparison of the solution temperature contours between the experimental results and the simulation results respectively for a PDMS/PDMS system and for a Glass/PDMS system. Fig 7-12a and Fig7-13a are the experiment results, and Fig 7-12b and Fig7-13b are the simulation results. It can be observed that, for both the PDMS/PDMS system and the Glass/PDMS system, the experimental results agree well with the theoretical predictions. Fig. 7-14 and Fig. 7-15 give the comparison of the solution temperature distribution along the flow direction near the T-section between the experimental results and the numerical predictions respectively for a PDMS/PDMS system and a Glass/PDMS system. From these two figures, it is found that the temperature difference between the experimental data and the numerical predictions is around $2.2\text{ }^{\circ}\text{C}$ (9 % of the total increment of solution temperature) at the inlet of mixing channel and $1.5\text{ }^{\circ}\text{C}$ (6% of the total increment of solution temperature) at downstream ($z/H = 9$) of the mixing channel for the PDMS/PDMS channel. Meanwhile, the temperature difference between the experiments and numerical predictions is less than $1\text{ }^{\circ}\text{C}$ (6% of the total increment of solution temperature) in the PDMS/Glass channel. This indicates the experimental results are quantitatively consistent with the numerical simulations. It suggests that the proposed mathematical models, the developed numerical scheme and the numerical code are reliable, and hence can be used for predicting and analyzing the Joule heating induced temperature

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field in the microfluidic channels. Taking a close examination to these two figures, it can be seen that the numerical predictions are tending to slightly overestimate the solution temperatures. The difference between the experimental results and the numerical predictions shifts from 2.2 °C (at the inlet of the mixing channel) to 1.5 °C (at the downstream ($z/H = 9$) of the mixing channel) for PDMS/PDMS channel. The presence of this discrepancy may be in part due to uncertainties in the temperature dependence of the material properties set in the numerical simulations, such as the thermal and electrical properties of the buffer solution (NaHCO_3). In addition, another reason for the uncertainty may be due to the non-uniform microchannel geometry at the T-section and downstream of the T-channel caused by fabrication process.

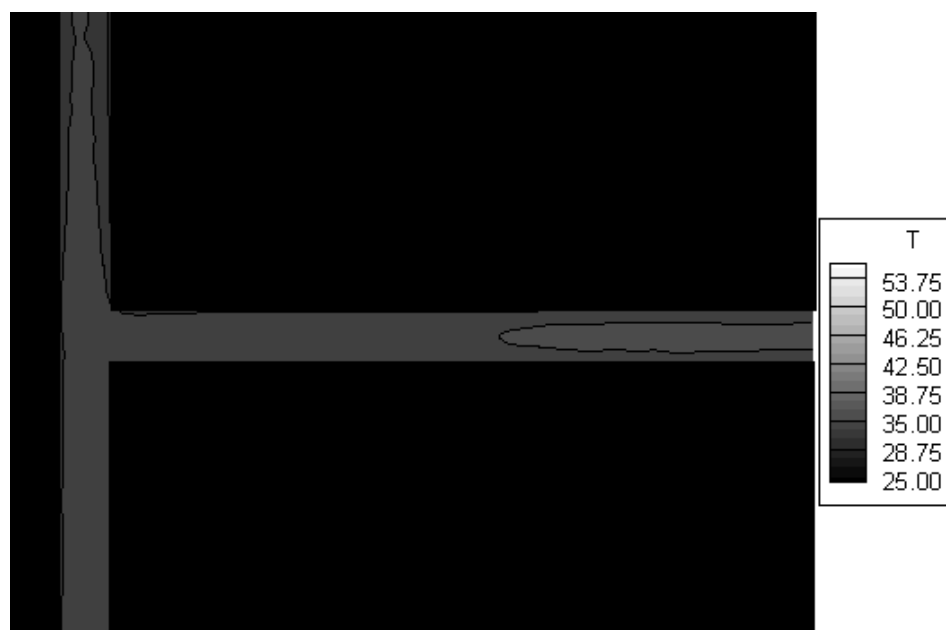


(a)



(b)

Fig. 7-12 Comparison of the solution temperature contours between the experimental results and the numerical simulations for a PDMS/PDMS system: (a) experiment results and (b) numerical simulations



(a)



(b)

Fig. 7-13 Comparison of the solution temperature contours between the experimental results and the numerical simulations for a Glass/PDMS system: (a) experiment results and (b) numerical simulations

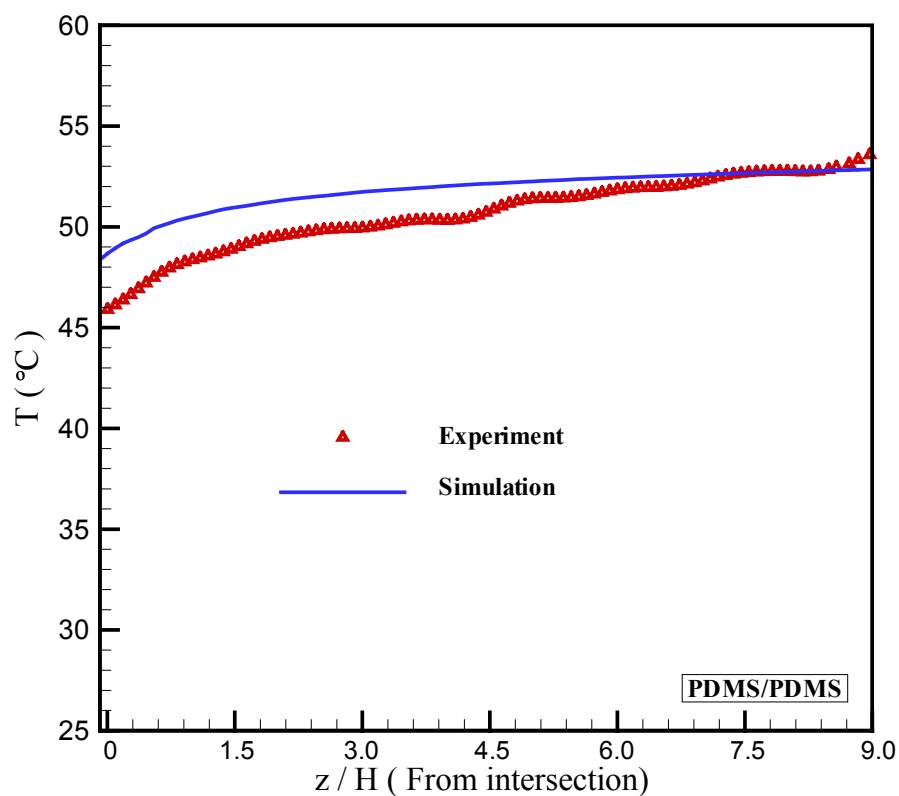


Fig. 7-14 Comparison of the solution temperature distribution along the flow direction near the T-section between the experimental results and the numerical simulations for a PDMS/PDMS system

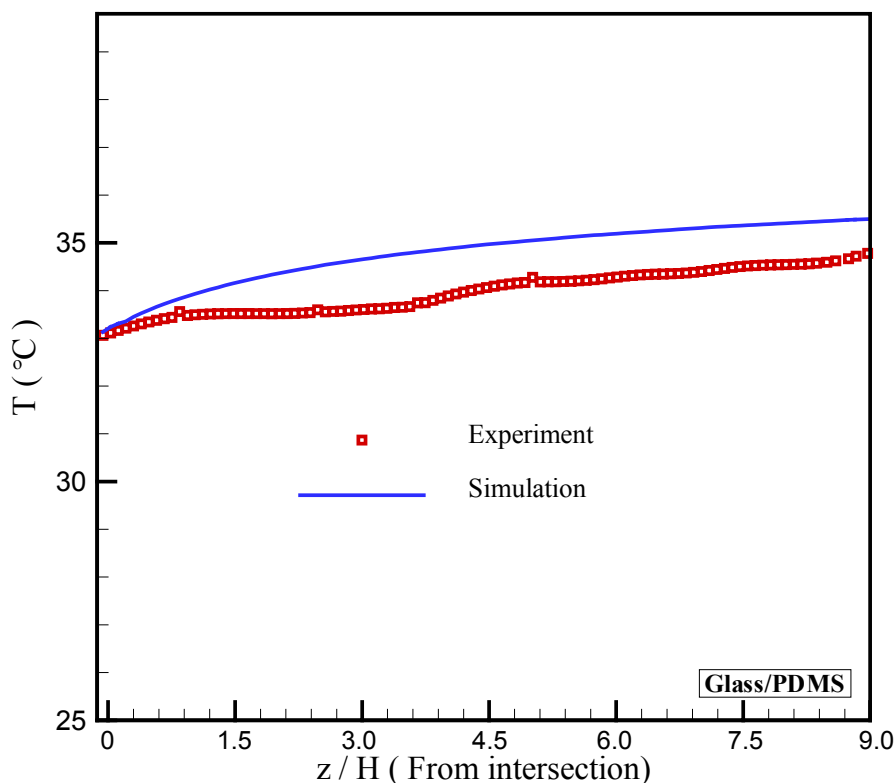


Fig. 7-15 Comparison of the solution temperature distribution along the flow direction near the T-section between the experimental results and the numerical simulations for a Glass/PDMS system

7.3.6 Uncertainties in the temperature measurements

The major uncertainties in the temperature measurements may include the background noise and photobleaching of the rhodamine dye. In the measurements, the average noise level in the experimental results was approximately ± 1 °C, which was reduced through the smoothing procedure discussed in thesis, and the observed repeatability was approximately ± 2 °C. Meanwhile, as earlier mentioned, in experiments, the second cold field image was compared to initial image and it was

found that the intensity values of the two images were identical, suggesting that the photobleaching of the rhodamine dye during the experiment was not significant.

In addition, the uncertainties also include the asymmetric structure at the channel/reservoir interfaces, created during the reservoir cutting process, and/or asymmetric channel geometry near the T-junction, as a result of the photoresist spin coating process.

7.4 Measurement of EOF without/with Joule heating effects in straight microchannels

7.4.1 Experimental technique

Micron-resolution Particle Image Velocimetry (Micro-PIV) is a technique that has been developed recently to measure the velocity of small scale flows in a spatially resolved manner (*Santiago, et al.*, 1998). Micro-PIV refers to the application of the PIV technique to measure velocity fields of fluid motion with length scales of order 100 microns, and with spatial resolution of individual velocity measurements of order 1 – 10 microns. The flow is illuminated by either a broad wavelength continuous light source, such as a mercury vapor lamp, or a pulsed laser, such as a frequency doubled Nd:YAG. Normally, Micro-PIV is used to measure the velocity of micro scale flows by measuring the motion of small tracer particles either naturally present in the flow or artificially added to the flow. Regardless of whether the fluid motion or particle motion is being studied, the technique is the same, which is commonly based on the techniques of cross-correlation, double frame, and double exposure.

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The small particles are observed with a microscope. Typically the particles are coated with a fluorescing dye to enable epi-fluorescent imaging. Images are captured with a precise time delay from one image to the next. A consecutive pair images is divided into many small interrogation regions. The corresponding interrogation regions from each of the two original images are cross-correlated to determine the most likely relative displacement of the particles in the interrogation regions in the form of a cross-correlation peak. Repeating this procedure thousands of times produces the spatially-resolved measurements of fluid or particle motion in the microfluidic system interested.

7.4.2 Chemicals preparation

Same as that in section 7.3.2, Sodium Bicarbonate (NaHCO_3) (Sigma, St. Louis, MO) solution was used as the work solution in the measurement of EOF. In order to measure the EOF profile without/with Joule heating effects, the concentrations of NaHCO_3 solution prepared for the experiment were 10^{-4} M (negligible Joule heating) and 50mM (with Joule heating), respectively.

The tracer particles used in the experiment were purchased from Duke Scientific (Diameter: $d_p = 0.93\mu\text{m}$; made of polystyrene). The particles have a maximum excitation wavelength of 540nm (green, very close to the characteristic wavelength of Nd: YAG) and a maximum emission wavelength of 610 nm (red). The concentration of fluorescent particles was around 2×10^9 particles/mL. The objective lens of the microscope was $20\times$ with $\text{NA}=0.45$. Under these conditions described above, we could obtain the total depth of correlation (Nguyen and Wereley, 2002):

$$\delta z_m = \frac{3n\lambda_0}{\text{NA}^2} + \frac{2.16d_p}{\tan \theta} + d_p = 18.93\mu\text{m} \quad (7-2)$$

where $\tan \theta \sim \sin \theta = NA/n$, $n = 4/3$, which is the refractive index of the fluid (here it is water) between the microfluidic device and the objective lens, and $\lambda_0 = 610\text{nm}$, which is the wavelength of the excited light in vacuum.

7.4.3 Micro-PIV system for measurement of EOF

The Micro-PIV setup consists of four main components: an illumination system, an optical system, a coupled charge device (CCD) camera and a control system. The control system consisting of a peripheral component interface (PCI) card, and its corresponding software, is implemented in a PC. The PC can control and synchronize all actions related to illumination and image recording. The schematic of the setup is illustrated in Fig. 7-16 (without including the control system).

A double pulsed Q-switched (quality switched) Nd:YAG laser is used for illumination. By including a Q-switch inside the cavity the laser can work in a triggered mode. The laser has a wavelength of 532 nm and a maximum energy of 160 mJ. The two-laser-head system allows the realization of two laser pulses with a very small delay. The system can work in different modes: single exposure in one frame, double exposure in one frame, and double exposure in double frames. In our experiments, the mode of double exposures in double frames is used because of the high signal-to-noise ratios and the better quality of the cross-correlation technique.

The optical system includes a Nikon inverted microscope (Model ECLIPSE TE2000-S) with a set of epi-fluorescent attachments. There are three optical elements in the filter cube: an excitation filter, a dichroic mirror and an emission filter. The emission filter is used in both measurements to select more specific the emission wavelength of the sample and to remove the traces of excitation light. The PIV-measurement uses an epi- fluorescent attachment of Nikon G-2E/C (an excitation

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filter for 540 nm, a dichroic mirror for 565 nm and an emission filter for 605 nm). Both filters in the attachment have a bandwidth of 25 nm.

An interline transfer CCD camera (Sony ICX 084) is used for recording the images. The resolution of the camera is 640 pixels $\times$ 480 pixels, with 12 bits grayscale. An interline transfer CCD camera (Sony ICX 084) is used for recording the images. The resolution of the camera is 640 pixels $\times$ 480 pixels. With a CCD sensor size of 6.3 mm $\times$ 4.8 mm, the size of the measured area is 320 μ m $\times$ 240 μ m and the image pixel spacing is 0.5 μ m. The spatial resolution, defined by the interrogation area is 16 pixels $\times$ 16 pixels for the whole region. This corresponds to a spatial resolution of 8.0 μ m $\times$ 8.0 μ m. The minimum inter-frame transfer time, and thus the fastest time delay for the two PIV images, is 500 ns. While in the measurements reported in this thesis, the temporal resolution of the micro-PIV measurement, which is defined as the time interval for taking back-to-back images (or the delay time of the two laser pulses), is 1.5 ms. To ensure that the CCD camera is working at its optimum temperature of -15°C , a cooling system is integrated in the CCD camera. In the mode of double exposure in double frames, the camera can record two frames of the flow fields and then digitizes them in the same image buffer.

7.4.4 Experimental results and discussion

Experiments were performed for fabricated straight microchannels with cross-sectional dimension of 100 $\times$ 100 μ m. The hybrid Glass/PDMS channels were used and the channel structure is illustrated in Fig. 7-1. The working fluids used in the experiment are NaHCO_3 solution with concentration of 10^{-4} M and 5×10^{-2} M. a voltage of 1200V was imposed across the channel with a length of 2cm, giving the

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applied electric field strength of 600V/cm. The images obtained in measurements were evaluated with PIVview software (PivTec GmbH).

Fig. 7-17 shows the experimental results of the Micro-PIV measurement for the electroosmotic velocity vector field of 10^{-4} M NaHCO_3 electrolyte in (a) the entry region of the channel and (b) the downstream region of the channel. The left figure is the snapshot image of the velocity vector field evaluated by the PIVview software; the right figure depicts the velocity vector field. It is observed that at the entry region of the channel (see Fig. 7-17 (a)) the flow exhibits a 2D structure with a transverse velocity component (v) towards the channel center. This indicates the flow is developing due to the reservoir effect. Moreover, it is also noted that the flow development ends within a distance of twice channel width along the flow direction. After that, the flow is found to reach its fully developed profile. This can be judged by a uniform or “plug-like” velocity profile. Such “plug-like” flow pattern is also shown in Fig. 7-17 (b), which depicts the velocity vector field in the downstream region of the channel. Nonetheless, based on the experimental results presented in Fig. 7-17, it can be concluded that under such experimental conditions, the Joule heating effect is negligible, which should be expected because of the dilute electrolyte concentration used.

Fig 7-18 shows the experimental results of the Micro-PIV measurement for the electroosmotic velocity vector field of 5×10^{-2} M NaHCO_3 electrolyte in (a) the entry region of the channel and (b) the downstream region of the channel. From Fig. 7-18(a), a 2D flow structure can still be observed at the channel entry because of the reservoir effect. The transverse velocity component (v) is found much stronger than that observed in Fig. 7-17(a). More importantly, even after the entry effect ends (with a distance of twice channel width along the flow direction, which is similar to what

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reported in Fig. 7-17(a)), the electroosmotic flow velocity is found not only to be increased (longer vector) but also to become non-uniform, deviating from its normal “plug-like” shape. It can be seen clearly that the electroosmotic flow velocity exhibits a concave shape in Fig.7-18(a) which shows the flow still under development and a convex shape in Fig. 7-18(b) which shows the flow is fully-developed. This scenario can be attributed to the Joule heating effects and has been discussed in the previous sections.

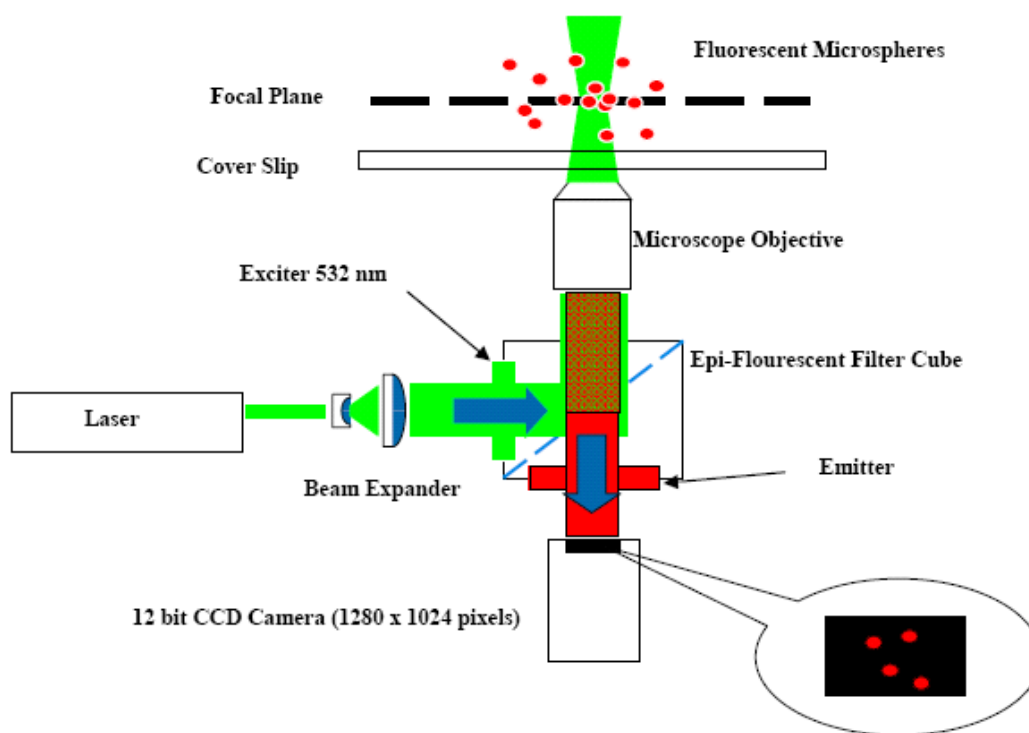
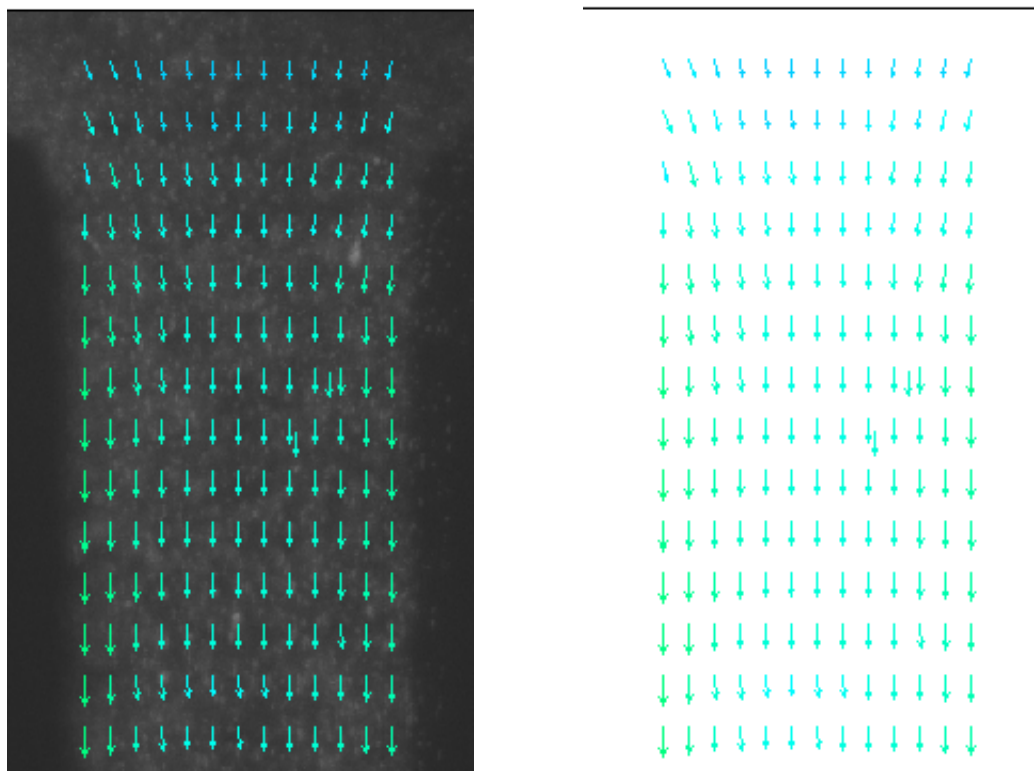
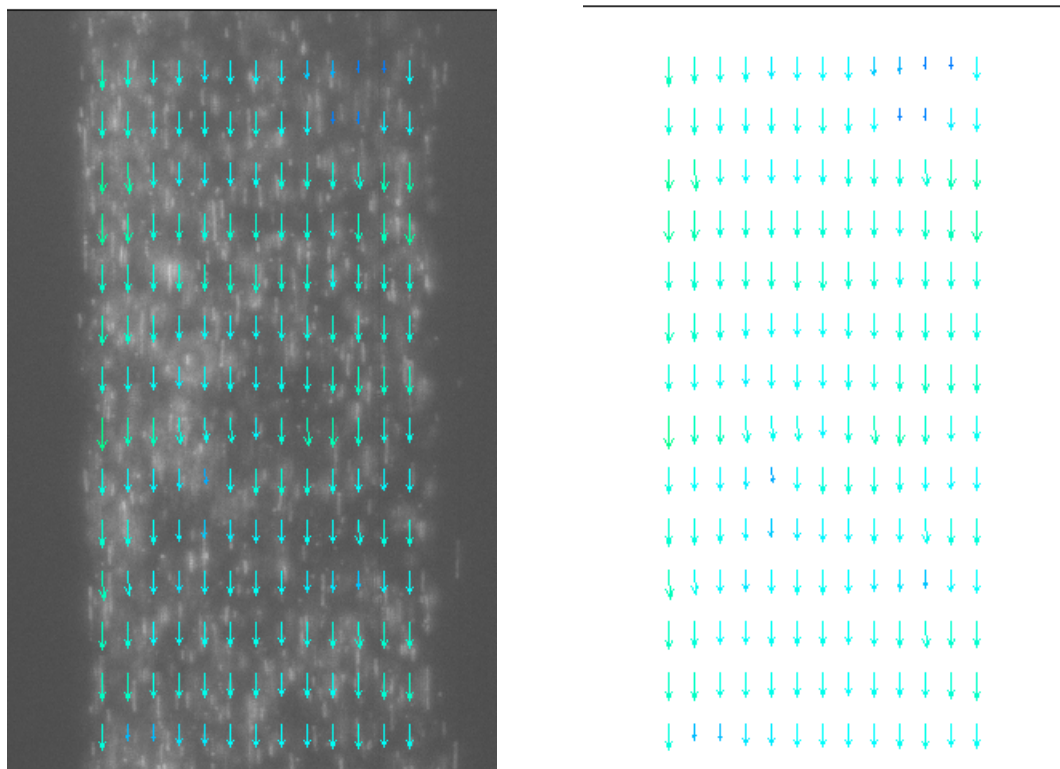


Fig. 7-16 Schematic diagram of the Micro-PIV system



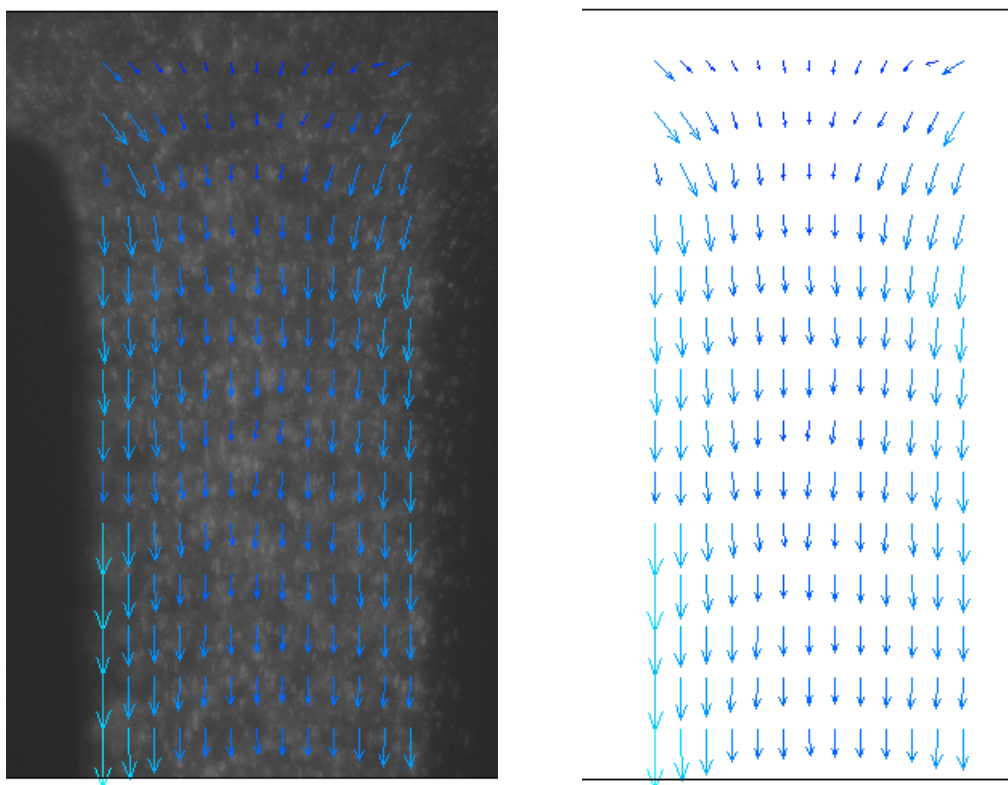
(a)

Fig. 7-17 Experimental results of the Micro-PIV measurement for electroosmotic velocity vector field of 10^{-4} M NaHCO_3 electrolyte in a hybrid Glass/PDMS microchannel under negligible Joule heating effects in (a) the entry region of the channel.



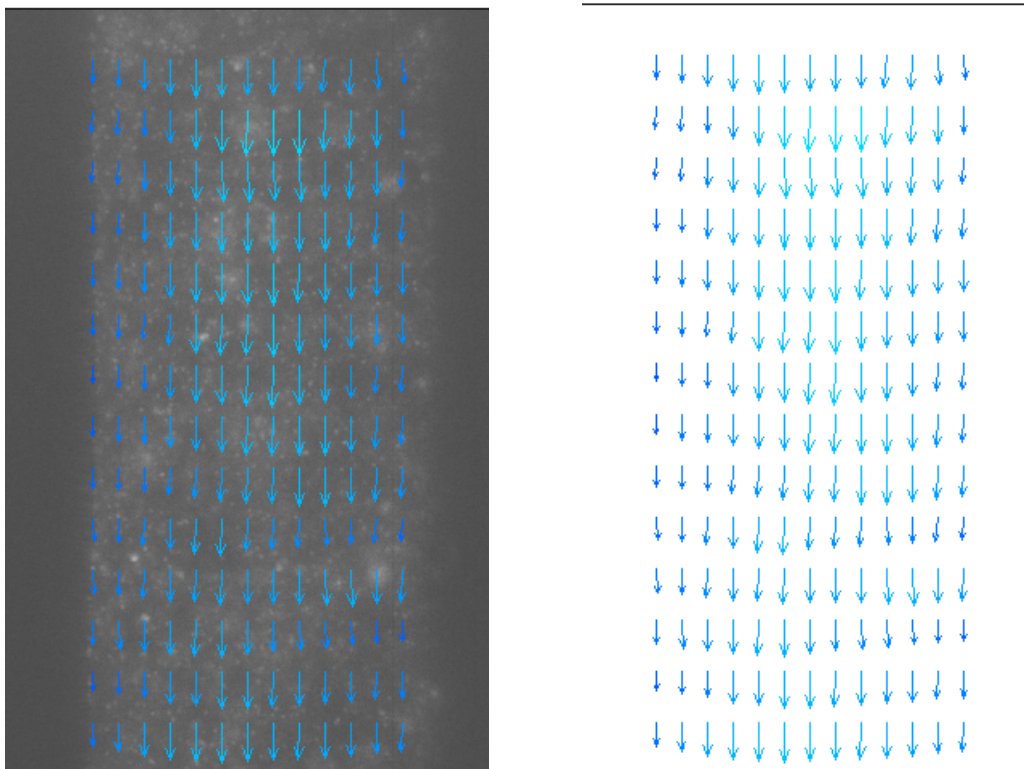
(b)

Fig. 7-17 Experimental results of the Micro-PIV measurement for electroosmotic velocity vector field of 10^{-4} M NaHCO_3 electrolyte in a hybrid Glass/PDMS microchannel under negligible Joule heating effects in (b) the downstream region of the channel.



(a)

Fig. 7-18 Experimental results of the Micro-PIV measurement for electroosmotic velocity vector field of 5×10^{-2} M NaHCO_3 electrolyte in a hybrid Glass/PDMS microchannel under Joule heating effects in (a) the entry region of the channel.



(b)

Fig. 7-18 Experimental results of the Micro-PIV measurement for electroosmotic velocity vector field of 5×10^{-2} M NaHCO_3 electrolyte in a hybrid Glass/PDMS microchannel under Joule heating effects in (b) the downstream region of the channel.

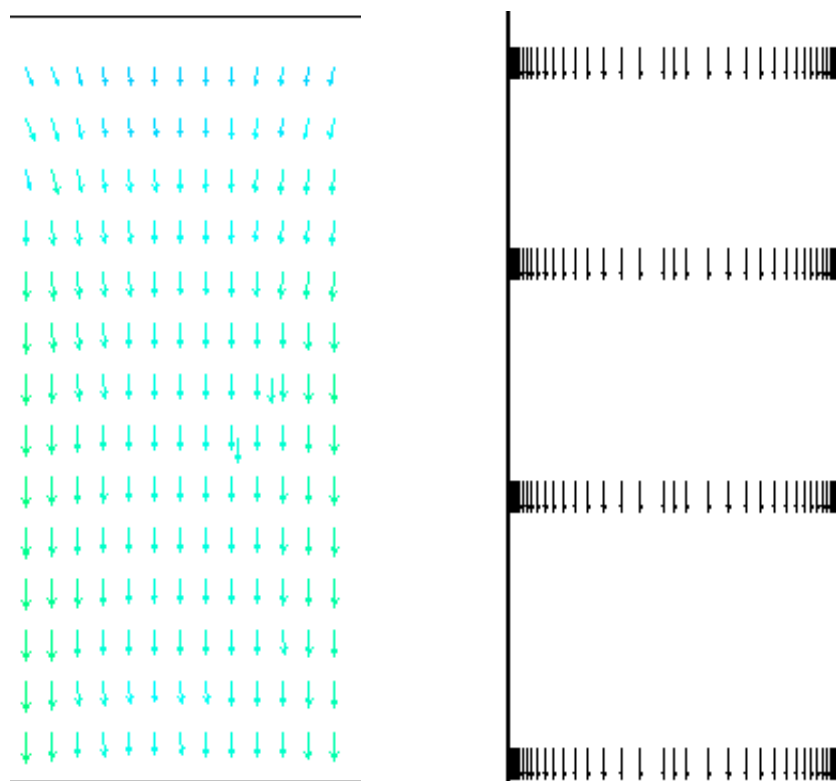
7.4.5 Comparison with numerical simulation results

Using the proposed mathematical models presented in chapter 6, the numerical simulations were carried out based on the same parameters as those used in the experiment. The parameters considered in computations are $E_0 = 600 \text{ V/cm}$,

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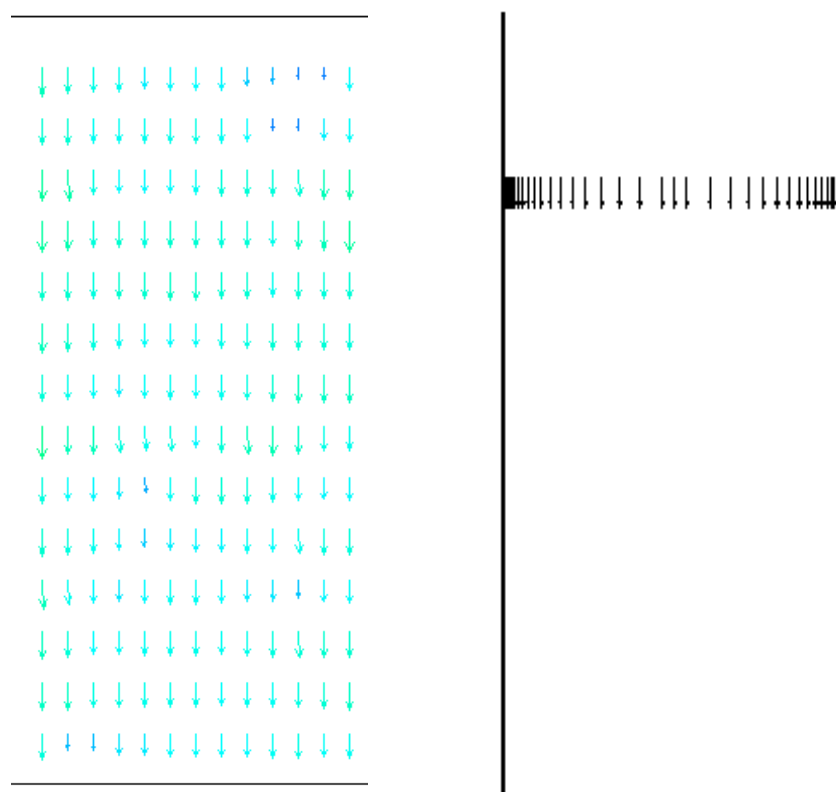
$h = 10W / m^2 K$ and two different concentrations $C = 50mM$ ($\zeta_1 = -50mV$), and $C = 0.1mM$ ($\zeta_2 = -75mV$). The comparison of the electroosmotic flow velocity vectors between the experimental measurements and the numerical predictions without Joule heating effect are shown in Fig. 7-19 for (a) the entry region of the channel and (b) the downstream region of the channel. The left figure and the right figure respectively represent the experimental measurements and numerical simulations. It should be pointed out that in the numerical simulation, the non-uniform grid is employed along the flow direction in order to capture the detailed information for the flow in the entry region. The grid in the entry region is denser than that in the downstream region of the channel. Therefore, only velocity vector at one point in the downstream region can be presented. The comparison of electroosmotic flow velocity distribution along the transverse direction between the experimental measurements and the numerical predictions without Joule heating effect are provided in Fig. 7-20 for (a) the entry region of the channel and (b) the downstream region of the channel. The error bars are based on twice the standard deviation of three independent measurements for each case. It can be found from Fig. 7-19 and Fig. 7-20 that the numerical simulations without considering the Joule heating effect agree well with the experiment results.

The comparison of the electroosmotic flow velocity between the experimental measurements and the numerical simulations with Joule heating effects are shown in Fig. 7-21 and Fig. 7-22 for (a) the entry region of the channel and (b) the downstream region of the channel. The error bars in Fig. 7-22 are based on twice the standard deviation of three independent measurements for each case. It can be clearly seen that the numerical simulation results are in good agreement with the experimental results in the presence of Joule heating effects.



(a)

Fig. 7-19 Comparison of the electroosmotic flow velocity vector between the experimental results and the numerical simulations without Joule heating effect in (a) the entry region of the channel.



(b)

Fig. 7-19 Comparison of the electroosmotic flow velocity vector between the experimental results and the numerical simulations without Joule heating effect in (b) the downstream region of the channel.

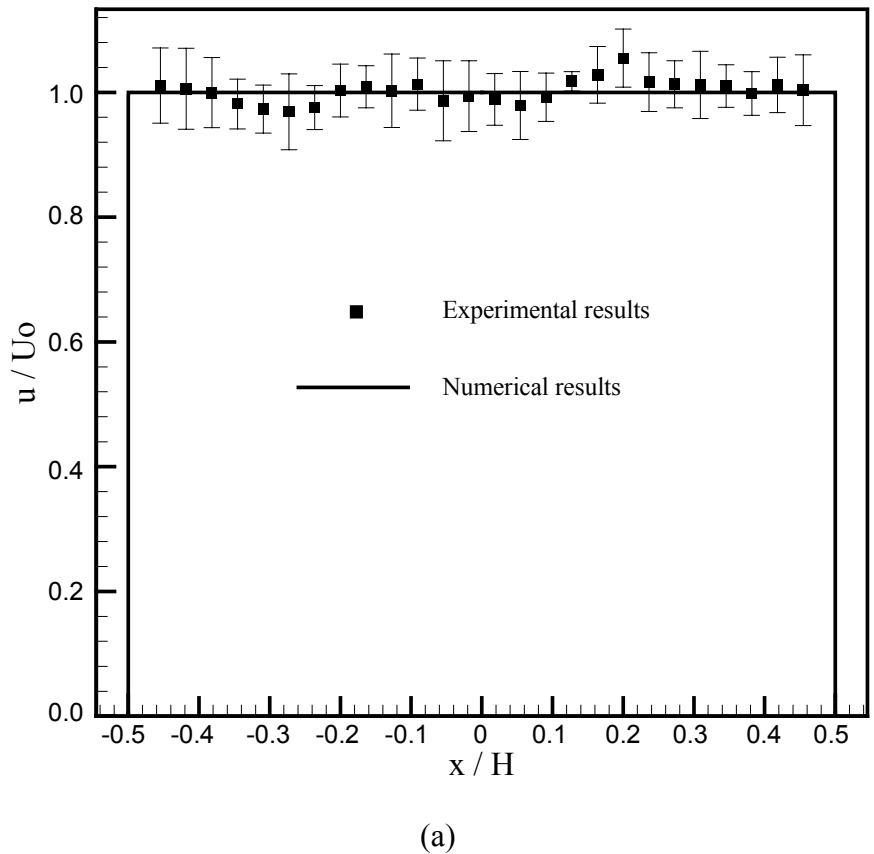
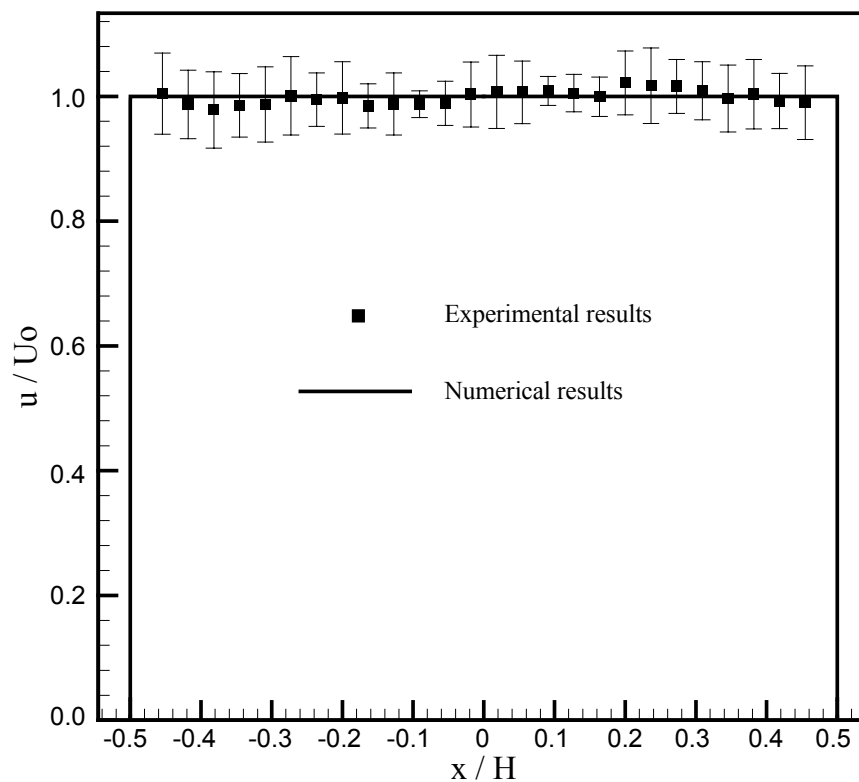


Fig. 7-20 Comparison of the electroosmotic flow velocity distributions along the transverse direction between the experimental results and numerical predictions without Joule heating effect in (a) the entry region of the channel.



(b)

Fig. 7-20 Comparison of the electroosmotic flow velocity distributions along the transverse direction between the experimental results and numerical predictions without Joule heating effect in (b) the downstream region of the channel.

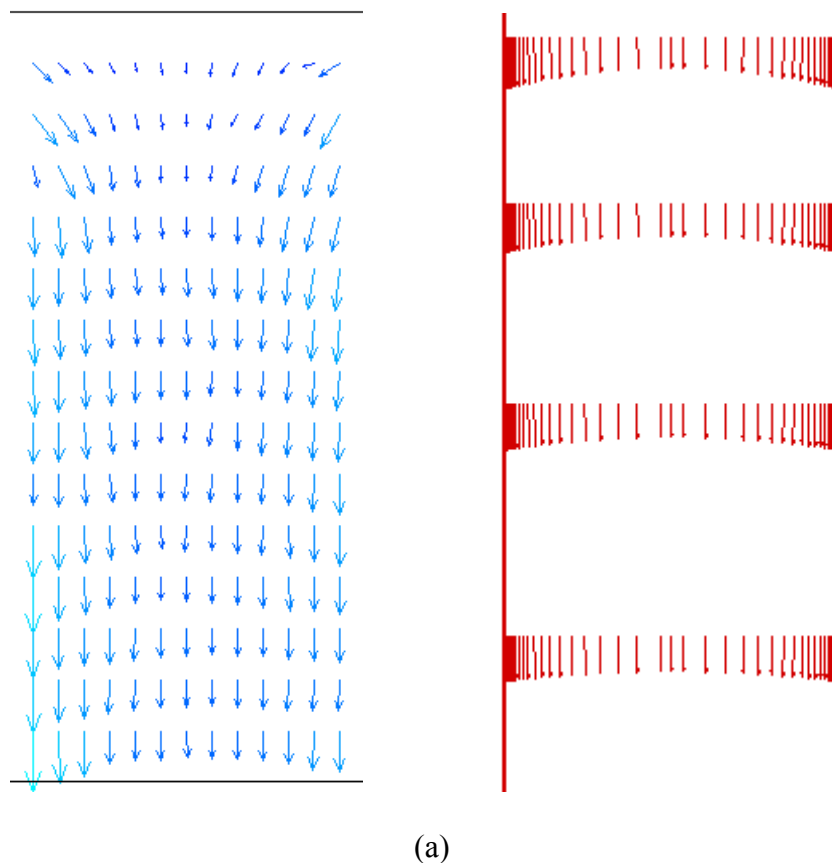
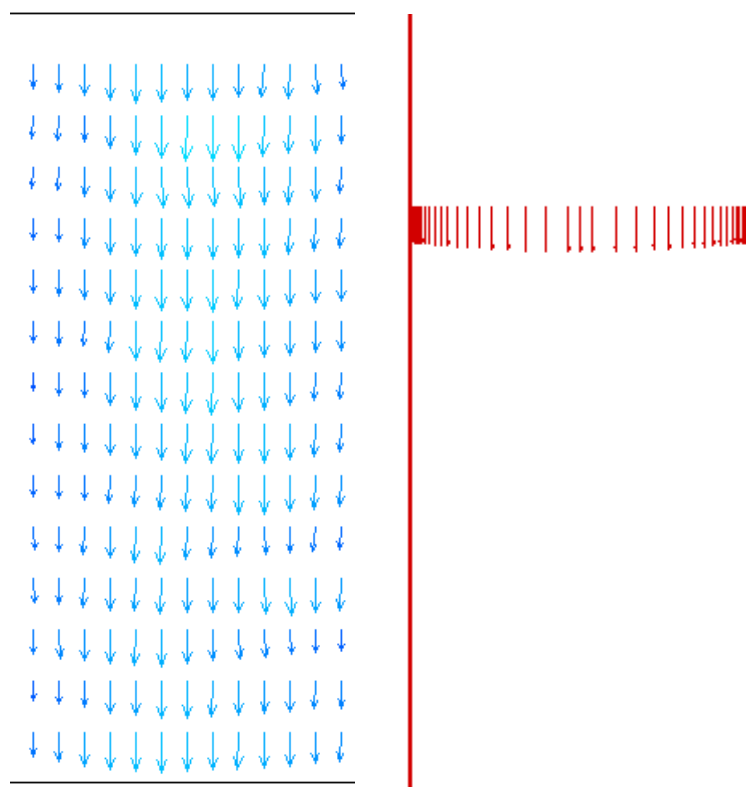
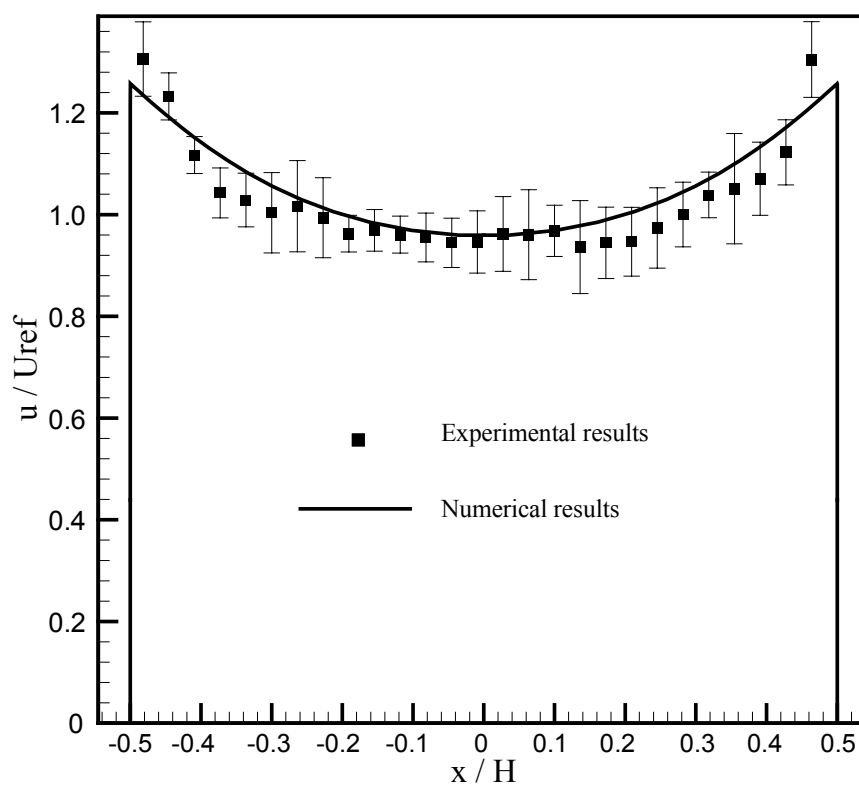


Fig. 7-21 Comparison of the electroosmotic flow velocity vector between the experimental results and the numerical simulations with Joule heating effect in (a) the entry region of the channel.



(b)

Fig. 7-21 Comparison of the electroosmotic flow velocity vector between the experimental results and the numerical simulations with Joule heating effect in (b) the downstream region of the channel.



(a)

Fig. 7-22 Comparison of the electroosmotic flow velocity distribution along the transverse direction between the experimental results and numerical predictions with Joule heating effect in (a) the entry region of the channel.

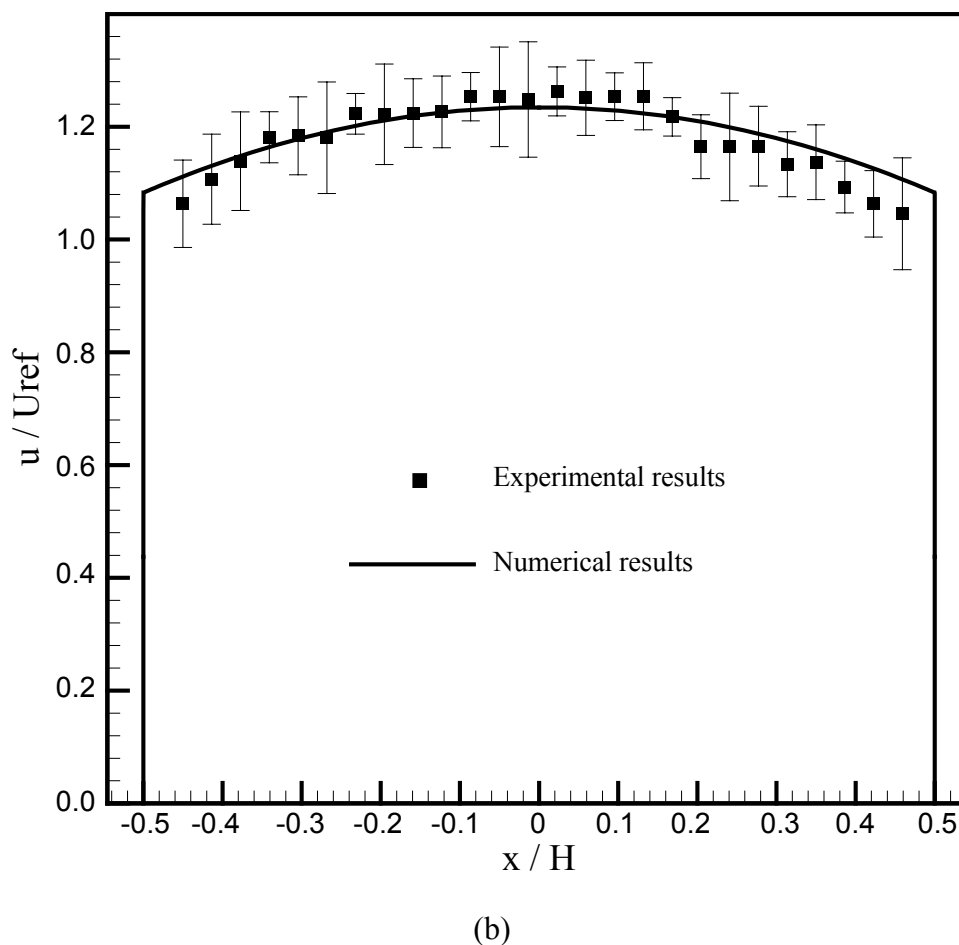


Fig. 7-22 Comparison of the electroosmotic flow velocity distribution along the transverse direction between the experimental results and numerical predictions with Joule heating effect in (b) the downstream region of the channel.

7.4.6 Uncertainties in the microPIV measurements

For the micro-PIV technique, the uncertainty is usually attributed to two major factors. One is the background noise due to the contribution of out-of-focus particles, also referred to as the focus depth of correlation. The detailed discussion of the focus

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depth matter can be found in the literature (*Nguyen and Wereley, 2002*). In order to obtain reliable measurements, the background noise was minimized by using high dynamic range CCD cameras, applying special image processing algorithms during interrogation, and limiting the number density of particles in the flow field in the current experiments. The other major uncertainty is due to the Brownian motion of tracer particles. In general, to achieve microscale spatial resolution, the particles are chosen small enough to follow the flow faithfully without (1) disrupting the flow field, (2) clogging the microdevice, and (3) producing unnecessarily large images. At the same time, the particles must be chosen large enough so that they scatter sufficient light to be recorded and sufficiently dampen out Brownian motion. In particular, the Brownian motion plays an important role when sub-micron tracer particles are used in PIV experiments with flow velocities of less than 1 mm/s. According to Probst (1994), the Brownian motion-induced random velocity u_b can be estimated from

$$u_b = \sqrt{2D_i / \Delta t_{PIV}} \quad (7-1)$$

Where, Δt_{PIV} is the time interval of the two laser pulses, and D_i is the mass diffusivity of dilute tracer particles.

The mass diffusivity of dilute tracer particles suspended in water is governed by the Einstein–Stokes equation (eg. equation (4-18a)). For the particles of 465 nm in radius, the time interval of 1500 μs , and at room temperature of 25 °C, the Brownian velocity is estimated as 26.4 $\mu m/s$. As a result, the measurement error due to the Brownian motion, is less 2% when the characteristic fluid velocity is around 1.5 mm/s.

7.5 Summary

In this chapter, the microchannels were designed and fabricated using rapid prototyping techniques, including the Photolithography technique for the master fabrication and Soft Lithography technique for the replication of PDMS microchannels. Then a new rhodamine B based thermometry technique developed by *Ross et al.* (2002), which allows direct “in-channel” measurements of liquid solution temperatures in microfluidic channels, was used to measure the solution temperature field in the T-shape channels fabricated by the PDMS/PDMS and Glass/PDMS substrates. In addition, the electroosmotic flow velocity fields with or without Joule heating effects in a straight microchannel were measured using a Micro particle image velocimetry (Micro-PIV) technique.

The experimental results were compared with the numerical simulations, and a reasonable agreement was found. This suggests that the proposed mathematical model, developed numerical scheme and in-house written numerical code presented in the previous chapters are valid and sufficient for predicting the Joule heating induced temperature field and its effects on the electroosmotic flow field.

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CONCLUSIONS AND FUTURE STUDIES

8.1 Conclusion and contributions made by this study

Following the objectives of this project, extensive and rigorous modeling on the electrokinetic mass transport with Joule heating effects in various microfluidic systems has been developed and numerically analyzed with various physicochemical conditions. Experiments on characterizing the Joule heating and its effect on the electroosmotic flow have been carried out in order to verify the developed mathematical model and proposed numerical method. A reasonable agreement between the experimental results and the numerical predictions has been obtained. An in-depth understanding of the Joule heating and its effects on electrokinetic transport phenomenon in microfluidic systems has been achieved. The major contributions made during the course of this thesis can be summarized as follows:

1. Development of the rigorous mathematical model: Comprehensive mathematical models describing the electrokinetic transport with Joule heating effects in microfluidic systems were formulated. The models developed in this study include the Poisson equation for the electric double layer potential distribution, Laplace equation for the externally applied electric potential, modified Navier-Stokes (N-S) equations for the motion of liquid driven by electrokinetic body forces, energy equation for the temperature field due to Joule heating. In addition, the ionic concentration distributions were considered as either governed by the Nernst-Planck (N-P) equation or described by the Boltzmann distribution. Since the phenomenological thermophysical coefficients including the dielectric constant in the

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Poisson equation, the liquid viscosity in the N-S equations and the energy equation, the electrical conductivity in the Laplace equation and the energy equation, the ionic diffusion coefficient in the N-P equation are dependent on temperature, the Poisson equation, the Laplace equation, the N-S equations, the energy equation, and the N-P equation (or Boltzmann distribution) are strongly coupled. Moreover, in view of the fact that electroosmotic flow is mainly used for delivering and separating chemical or biological samples, the mass species transport equation was therefore added into the model development to examine the Joule heating effect.

2. Validation of the Boltzmann distribution (versus the Nernst-Planck equation): A numerical study was conducted to evaluate the ionic concentration distributions in both the developing and the fully developed *EOF* regions on the basis of the Nernst-Planck equation and the Boltzmann distribution. It can be concluded that for low values of κR , where the *EDL* plays an important role, in the *EOF* developing region the ionic concentration distribution predicted by the Nernst-Planck equation deviates from that by the Boltzmann distribution. As the *EOF* develops, the deviation becomes smaller, and finally in the *EOF* fully developed region, the Nernst-Planck equation predicts the same ionic concentration distribution as that predicted by the Boltzmann distribution. For large values of κR , where the *EDL* regime is thin compared to the capillary radius, the Nernst-Planck equation and the Boltzmann distribution predicts identical ionic concentration distributions in both developing and developed regions of the *EOF*. These findings suggest that as for the Joule heating is concerned where the κR usually is large, the simple Boltzmann distribution can be assumed.

3. Joule heating and its effects in the commercial capillary electrophoresis system (2D axial-symmetric channels) with a thermostated cooling mode:

Rigorous mathematical models for describing the transient Joule heating induced temperature field and its effect on the electroosmotic flow and electrokinetic transport of sample species in the commercial capillary electrophoresis system with thermostated cooling system were numerically solved by using the finite-volume-based CFD technique. The simulations demonstrated that due to the coupling between the *EOF* field and the temperature field, the *EOF* has almost the same entrance length as the Joule heating induced temperature development. The Joule heating causes the development of both radial and axial temperature distributions in the capillary. It was found that the Joule heating effect is significant for large-sized capillaries, concentrated buffer solutions, high applied electric field strengths, and less effective cooling modes outside the capillary. In addition, it was shown that the presence of Joule heating could have a great impact on the electroosmotic flow and sample species transport. Not only it causes the *EOF* to deviate from its normal flat profile, i.e. cause the *EOF* exhibit a concaved shape in the developing region and a parabolic pattern in the fully developed region, but also it makes the sample species axially transport faster and more dispersive along the radial direction of the capillary (i.e. deviate from its flat translating interface or plug-like sample band shape).

4. Joule heating and its effects in the 3D rectangular microfluidic channels with a natural air convection cooling mode:

Thorough numerical analyses were conducted for the Joule heating and its effects in the rectangular microfluidic channels with a natural air convection cooling mode. Various 3D microfluidic structures were considered in the computation, including straight channels (both commercial and

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fabricated using Glass/PDMS and PDMS/PDMS substrates), T-shape microchannels fabricated using Glass/PDMS and PDMS/PDMS substrates, and channels with a step change of cross-section fabricated using Glass/PDMS and PDMS/PDMS substrates.

The simulations showed that due to the low heat transfer coefficient of natural air convection cooling mode, the entrance length of the electroosmotic flow and the Joule heating induced temperature developments in rectangular channels is much larger than that in cylindrical capillaries but with the high heat transfer coefficient of thermostated cooling mode (discussed in chapter 5). Under such a situation, the transverse variation of solution temperature is negligible as compared to the Joule heating induced temperature increment. Furthermore, an unusual heat transfer behavior was observed. When the inner dimension of channels was kept unchanged, it was found that increasing channel wall thickness would result in lower liquid temperatures. Nevertheless, it was concluded that the Joule heating effect is more significant for the system with larger Joule number, thinner wall and poorer thermal conductivity of substrates.

The simulations also showed that the presence of Joule heating effects causes the electroosmotic flow deviate from its flat profile; the electroosmotic velocity exhibits a concave shape in the developing region and a convex shape in the fully developed region. Correspondingly, the sample band shape for the case of the dispersion of a finite sample plug is distorted.

The simulation for the T-shape channels provided the detailed information and full understanding of the Joule heating induced temperature field and its effects on the electroosmotic velocity field. It was also shown that the Joule heating effect could enhance the electrokinetically driven sample mixing in the T-shape microchannels.

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5. Experimental verification: In the experiment section, the straight and T-shape microchannels were designed and fabricated using rapid prototyping techniques, including the Photolithography technique for the master fabrication and Soft Lithography technique for the replication of PDMS microchannels. Then a new Rhodamine B based thermometry technique developed by *Ross et al.* (2002), which allows direct “in-channel” measurements of liquid solution temperatures in microfluidic channels, was used to measure the solution temperature field in the T-shape channels fabricated by the PDMS/PDMS and Glass/PDMS substrates. In addition, the electroosmotic flow velocity fields with or without Joule heating effects in a straight microchannel were measured using a Micro particle image velocimetry (Micro-PIV) technique.

The experimental results were compared with the numerical simulations, and a reasonable agreement was found. This suggests that the proposed mathematical model, developed numerical scheme and in-house written numerical code presented in the previous chapters are valid and sufficient for predicting the Joule heating induced temperature field and its effects on the electroosmotic flow field.

8.2 Recommendations for future studies

Based on the results presented in this study, some recommendations are made as following for future research in order to achieve a better and more complete understanding of the electrokinetic transport phenomena in microfluidic systems.

1. In chapter 2, for analyzing the electrokinetic sample transport, the assumptions were made for no adsorption of sample species onto the capillary wall and no interaction between sample species and the electrolyte solution components. The driving force for the electroosmotic flow in microchannels is determined by the

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local net charge density and the applied electric field. The net charge density is dependent on the EDL field and hence on the zeta potential; the magnitude of the electroosmotic flow in turn is governed by the zeta potential. Generally the zeta potential is a function of the ionic valence, the ionic concentration of the electrolyte solution, and the surface properties of the microchannel wall. For simplification, a system with a simple electrolyte solution and a homogeneous channel wall, zeta potential can be considered as constant. However, in practice, when the sample species is transported in the channel by mean of electrokinetic transport, the adhesion of these sample species to the channel wall will cause the non-uniform zeta potential distribution along the channel. Meanwhile, the interaction between the sample species and the electrolyte components also leads to a change of the physicochemical properties of the electrolyte. Therefore, the understanding of the electrokinetic transport behavior in such a situation is also important for manipulating the flow in microfluidic devices. But such complicated issue poses a great challenge.

2. As pointed out in chapter 6, the present study is mainly focus on the negative aspects the Joule heating effects. However, as mentioned in chapter 1, there are some positive aspects of the Joule heating effects such as to precisely control the temperature in microfluidic devices. One of the potential applications is to control the concentration gradient by precisely controlling the Joule heating induced solution temperature and temperature gradient. Concentration gradient generation in microfluidic structures is also of great importance to the biological and chemical analyses, such as chemotaxis for electrokinetic manipulation of cell motion (*Weiner et al.*, 1999, *Dekker and Segal*, 2000), and nucleation and growth of crystals (*Gallardo et al.*, 1999). The presence of Joule heating not only can

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cause temperature increase but also induce temperature gradient. The change of liquid temperature and the presence of temperature gradient would have an impact on characteristics of the concentration gradient. Therefore, utilizing the Joule heating is a very valid route to precisely control the solution temperature so as to control the concentration gradient in microfluidic systems.

3. Joule heating and its effects on electroosmotic flow and electrokinetic mass transport were examined for simple microfluidic structures including straight channels and T-shape channels, Further studies of electrokinetic transport with Joule heating effects can be conducted for one or two cross-joined channels, which is of practical importance to microfluidics based sample dispensing and separation.
4. In his research, what the author is dealing with is a coupled, multi-dimensional problem including the velocity field, electric field, temperature field and complex boundary conditions. No analytical expression for the Joule heating induced thermal entrance length of the electrokietc flow can be derived. However, it would be useful to get some generalized correlations to characterize the thermal entrance length in the presence of Joule heating based on some reasonable simplifications. This will also be a tremendous challenge to the future studies.

REFERENCES

REFERENCES

Ajdari, A., Generation of transverse fluid currents and forces by an electric field: electro-osmosis on charge-modulated and undulated surfaces, *Physical Review E*, 53 (1996) 4996-5005.

Arulanandam, S. and Li, D., Liquid transport in rectangular microchannels by electroosmotic pumping, *Colloids Surfaces A*, 161 (2000) 89-102.

Arulanandam, S. and Li, D., Determining ζ potential and surface conductance by monitoring the current in electro-osmotic flow, *J. Colloid Interface Sci.*, 225 (2000) 421-428.

Balss, K.M., Vreeland, W.N., Phinney, K.W. and Ross, D., Simultaneous concentration and separation of enantiomers with chiral temperature gradient focusing, *Anal. Chem.*, 76 (2004) 7243-7249.

Barragán, V.M. and Bauzá, C.R., Electroosmosis through a cation-exchange membrane: effect of an ac perturbation on the electroosmotic flow, *J. Colloid Interface Sci.*, 230 (2000) 359-366.

Beard, D.A., Taylor dispersion of a solute in a microfluidic channel, *Journal of Applied Physics*, 89 (2001) 4667-4669.

Beard, D.A., Response to "Comment on 'Taylor dispersion of a solute in a microfluidic channel'", *Journal of Applied Physics*, 90 (2001) 6555-6556.

Ben, Y. and Chang, H.-C. Nonlinear Smoluchowski slip velocity and vortex generation, *J. Fluid Mech.*, 461 (2002), 229-238.

Bianchi, F., Ferrigno, R. and Girault, H.H., Finite element simulation of an electroosmotic driven flow division at a T-junction of microscale dimensions, *Anal. Chem.*, 72 (2000) 1987-1993.

Bier, M., Palusinski, O.A., Mosher, R.A. and Saville, D.A., Electrophoresis: mathematical modeling and computer simulation, *Science*, 219 (1983), 1281-1287.

Boland, M., Arce, P. and Erdmann, E., Free convection flows in the fibrous or porous media: a solution for the case of homogeneous heat sources, *Int. Comm. Heat Mass Transfer*, 27-6 (2000) 745-754.

Bosse, M.A. and Arce, P., The role of Joule heating in dispersive mixing effects in electrophoretic cells: hydrodynamic considerations, *Electrophoresis*, 21 (2000) 1018-1025.

REFERENCES

- Bosse, M.A. and Arce, P., Role of Joule heating in dispersive mixing effects in electrophoretic cells: convective-diffusive transport aspects, *Electrophoresis*, 21 (2000) 1026-1033.
- Bousse, L., Cohen, C., Nikiforov, T., Chow, A., Kopf-Sill, A.R., Dubrow, R. and Parce, J.W., Electrokinetically controlled microfluidic analysis systems, *Annu. Rev. Biophys. Biomol. Struct.*, 29 (2000) 155-181.
- Burgreen, D. and Nakache, F.R., Electrokinetic flow in ultrafine capillary slits, *J. Phys. Chem.*, 68 (1964) 1084-1091.
- Chaudhari, A.M., Woudenberg, T.M., Albin, M. and Goodson, K.E., Transient liquid crystal thermometry of microfabricated PCR vessel arrays, *J. MEMS*, 7(4) (1998) 345-355.
- Chaudhury, M.K. and Whitesides, G.M., Direct measurement of interfacial interactions between semispherical lenses and flat sheets of poly(dimethylsiloxane) and their chemical derivatives, *Langmuir*, 7(1991) 1013-1025.
- Chidambara Raj, C.B. and Hunter, J.B., Analysis of Joule heating in electrophoretic processes, *Int. Comm. Heat Mass Transfer*, 18 (1991) 843-852.
- Coufal, P., Štulík, K., Claessens, H.A. and Cramers, C.A., The magnitude and reproducibility of the electroosmotic flow in silica capillary tubes, *J. High Resol. Chromatogr.*, 17 (1994) 325-334.
- Crank, J. and Nicolson, P., A practical method for numerical evaluation of solutions of partial differential equations of the heat-conduction type *Proc. Cambridge Philos. Soc.* 43 (1947) 50-67. [Re-published in: John Crank 80th birthday special issue in 1997 *Adv. Comput. Math.* 6 207-226.
- Cross, R.F., Joule heating calculations in capillary zone electrophoresis, *J. Chromatography*, 907 (2001) 357-360.
- Culbertson, C.T., Ramsey, R.S. and Ramsey, J.M., Electroosmotically induced hydraulic pumping on microchips: differential ion transport, *Anal. Chem.*, 72(2000) 2285-2291.
- Cummings, E.B., Griffiths, S.K., Nilson, R.H. and Paul, P.H., Conditions for similitude between the fluid velocity and electric field in electroosmotic flow, *Anal. Chem.*, 72 (2000) 2526-2532.
- Dasgupta, P.K. and Liu, S., Electroosmosis: A reliable fluid propulsion system for flow injection analysis, *Anal. Chem.*, 66 (1994) 1792-1798.
- Davis, K.L., Liu, K.L.K., Lanan, M and Morris, M.D., Spatially resolved temperature

REFERENCES

measurements in electrophoresis capillaries by Raman thermometry, *Anal. Chem.*, 65(1993) 293-298.

Debesset, S., Hayden, J.C., Dalton, C., Eijkel, J.C.T. and Manz, A., An AC electroosmotic micropump for circular chromatographic applications, miniaturisation for chemistry, biology & bioengineering, *Lab on a Chip*, 4 (2004) 396-400.

Dekker L.V. and Segal A.W., Signal transduction - signals to move cells, *Science*, 287(2000) 982-985.

De Mello, A.J., Habgood, M., Lancaster, N.L., Welton, T. and Wooton, R.C.R., Precise temperature control in microfluidic devices using Joule heating of ionic liquids, *Lab on a Chip*, 4 (2004) 417-419.

Dertinger, S.K.W., Chiu, D.T., Jeon, N.L. and Whitesides, G.M., Generation of gradient having complex shapes using microfluidic networks, *Anal. Chem.*, 73 (2001) 1240-12246.

Dorfman, K.D. and Howard, B., Comment on "Taylor dispersion of a solute in a microfluidic channel", *Journal of Applied Physics*, 90 (2001) 6553-6554.

Douglas, Jr.J. and Gunn, J., A general formulation of alternating direction methods, part I: parabolic equation and hyperbolic problems, *Numer. Math.*, 6 (1964) 428-453.

Dovich, N.J. and Zhang, J.Z., How capillary electrophoresis sequenced the human genome, *Angew. Chem. Int. Ed.*, 39 (2000) 4463-4468.

Duffy, D.C., McDonald, C., Schueller, O.J.A. and Whitesides, G.M., Rapid prototyping of microfluidic systems in poly (dimethylsiloxane), *Anal. Chem.*, 70 (1998) 4974-4984.

Dutta, D. and Leighton, D. T., Dispersion reduction in pressure-driven flow through microetched channels, *Anal. Chem.*, 73 (2001) 504-513.

Dutta, D. and Leighton, D. T., A low dispersion geometry for microchip separation devices, *Anal. Chem.*, 74 (2002) 1007-1016.

Dutta, D. and Leighton, D. T., Dispersion in large aspect ratio microchannels for open-channel liquid chromatography, *Anal. Chem.*, 75 (2003a) 57-70.

Dutta, D. and Leighton, D. T., Dispersion reduction in open-channel liquid electrochromatographic columns via pressure-driven back flow, *Anal. Chem.*, 75 (2003b) 3352-3359.

EL-Hakim, M.A., Viscous dissipation effects on MHD free convection flow over a nonisothermal surface in a micropolar fluid, *Int. Comm. Heat Mass Transfer*, 27-4

REFERENCES

(2000) 581-590.

Erickson, D., Li, D. and Werner, C., An improved method of determining the zeta potential and surface conductance, *J. Colloid Interface Sci.*, 232 (2000) 186-197.

Erickson, D. and Li, D., Numerical simulations of low power microchannel thermal cycling reactor, *Int. J. Heat Mass Transfer*, 45 (2002) 3759-3770.

Erickson, D. and Li, D., Influence of surface heterogeneity on electrokinetically driven microfluidic mixing. *Langmuir*, 18 (2002), 1883-1892.

Erickson, D., Sinton, D. and Li, D., Joule heating and heat transfer in poly (dimethylsiloxane) microfluidic systems, *Lab on a Chip*, 3 (2003) 141-149.

Ermakov, S.V., Zhukov, M.Yu., Capelli, L and Righetti, P.G., Experimental and theoretical study of artifactual peak splitting in capillary electrophoresis, *Anal. Chem.*, 66(1994) 4034-4042.

Ermakov, S.V., Zhukov, M.Yu., Capelli, L and Righetti, P.G., Artifactual peak splitting in capillary electrophoresis. 2. Defocusing phenomena for ampholytes, *Anal. Chem.*, 67 (1995a) 2957-2965.

Ermakov, S.V., Zhukov, M.Yu., Capelli, L and Righetti, P.G., On the measurements of electrophoretic mobilities by means of capillary isotachopheresis at a constant voltage, *Electrophoresis*, 16(1995b) 2149-2158.

Ermakov, S.V., Zhukov, M.Yu., Capelli, L and Righetti, P.G., Isotachopheresis at pH extremes: Theory and experimental validation, *Electrophoresis*, 19(1998) 192-205.

Ermakov, S.V., Jacobson, S.C. and Ramsey, J.M., Computer simulations of electrokinetic transport in microfabricated channel structures, *Anal. Chem.*, 70 (1998) 4494-4504.

Fan, Z.H. and Harrison, D.J., Micromachining of capillary electrophoresis injectors and separators on glass chips and evaluation of flow at capillary intersections, *Anal. Chem.*, 66 (1994) 177-184.

Freemantle, M., Downsizing chemistry, *Science/Technology*, 77(1999) 27-36.

Fu, L.-M., Lin, J.-Y. and Yang, R.-J., Analysis of electroosmotic flow with step change in zeta potential, *J. Colloid Interface Sci.*, 258(2003) 266-275.

Fu, L.-M., Yang, R.-J., and Lee, G.-B., Electrokinetic focusing injection methods on microfluidic devices, *Anal. Chem.*, 75 (2003) 1905-1910.

Fu, L.-M., Yang, R.-J., Lin, C.-H. and Y.-S. Chien, A novel microfluidic mixer utilizing electrokinetic driving forces under low switching frequency, *Electrophoresis*, 26 (2005)

REFERENCES

1814-1824.

Gallardo B.S., Gupta V.K., Eagerton F.D., Jong L.I., Craig V.S., Shah R.R. and Abbott N.L., Electrochemical principles for active control of liquids on submillimeter scales, *Science*, 283 (1999) 57 – 60.

Glasgow, I., Batton, J. and Aubry, N., Electroosmotic mixing in microchannels, *Lab on a Chip*, 4 (2004) 558-562.

Gleeson, J.P., Electroosmotic microfluidic flows with random zeta potential: modeling and simulation of microsystems, *J. Colloid Interface Sci.*, 248 (2001) 190-193.

Gleeson, J.P., Electroosmotic flows with random zeta potential, *J. Colloid Interface Sci.*, 249 (2002) 217-226.

Gobie, W.A. and Ivory, C.F., Thermal model of capillary electrophoresis and a method for counteracting thermal band broadening, *J. Chromatography*, 516 (1990) 191-210.

Griffiths, S.K. and Nilson, R.H., Electroosmotic fluid motion and late-time solute transport for large zeta potentials, *Anal. Chem.*, 72 (2000) 4767-4777.

Grushka, E., McCormick, R.M. and Kirkland, J.J., Effect of temperature gradients on the efficiency of capillary zone electrophoresis separations, *Anal. Chem.*, 61 (1989) 241-246.

Harrison, D.J., Manz, A., Fan, Z., Lüdi, H. and Widmer, H.M., Capillary electrophoresis and sample injection systems integrated on a planar glass chip, *Anal. Chem.*, 64 (1992) 1926-1932.

Harrison, D.J., Fluri, K., Seiler, K., Fan, Z., Effenhauser, C.S. and Manz, A., Micromachining a miniaturized capillary electrophoresis-based chemical analysis system on a chip, *Science*, 261 (1993) 895.

Heiger, D.N., *High Performance Capillary Electrophoresis: An Introduction*. France: Hewlett-Packard Company, 1992.

Heineman, W.R., Thomas, J.H., Wijayawardhana, A., Halsall, H.B., Ridgway, T.H., Choi, J.W. and Oh, K.W., BioMEMS: Electrochemical immunoassay with microfluidic systems, *Anal. Sci.*, 17 (2001) 281-284.

Herr, A.E., Molho, J.I., Santiago, J.G., Mungal, M.G. and Kenny, T.W., Electroosmotic capillary flow with nonuniform zeta potential, *Anal. Chem.*, 72 (2000) 1053-1057.

Herr, A.E., Molho, J.I., Drouvalakis, K.A., Mikkelsen, J.C., Utz, P.J. Santiago, J.G. and Kenny, T.W., On-chip coupling of isoelectric focusing and free solution electrophoresis for multidimensional separations, *Anal. Chem.*, 75 (2003) 1180-1187.

REFERENCES

- Hiemenz, P.C., Principles of Colloid and Surface Chemistry, 2nd ed Marcel Dekker, New York, 1986.
- Horiuchi K. and Dutta P., Joule heating effects in electroosmotically driven microchannel flows, *Int. J. Heat Mass Transfer* 47 (2004) 3085-3095.
- Hsu, J.P., Kao, C.Y., Tseng, S. and Chen, C.J., Electrokinetic flow through an elliptical microchannel: effects of aspect ratio and electrical boundary conditions, *J. Colloid Interface Sci.*, 248 (2002) 176-184.
- Hu, L.G., Harrison, D. J. and Masliyah, J.H., Numerical model of electrokinetic flow of capillary electrophoresis, *J. Colloid Interface Sci.*, 215 (1999) 300-312.
- Hunter, R.J., Zeta Potential in Colloid Science: Principles and Applications, Academic Press, New York, 1981.
- Incropera, F.P., and DeWitt, D.P., Fundamentals of heat and mass transfer, John Wiley & Sons, New York, 2002
- Ismagilov, R.F., Stroock, A.D., Kenis, P.J.A. and Whitesides, G.M., Experimental and theoretical scaling laws for transverse diffusive broadening in two-phase laminar flows in microchannels, *Applied Physics Letters*, 76 (2000) 2376-2378.
- Jones, A.E. and Grushka, E., Nature of temperature gradient in capillary zone electrophoresis, *J. Chromatography*, 466 (1989) 219-225.
- Jorgenson, J.W. and Lukacs, K.D., Zone electrophoresis in open-tubular glass capillaries, *Anal. Chem.*, 53 (1981), 1298-1302.
- Jorgenson, J.W. and Lukacs, K.D., Capillary zone electrophoresis, *Science*, 222 (1983), 266-272.
- Jung, B., Bharadwaj, R. and Santiago, J. G., Thousandfold signal increase using field-amplified sample stacking for on-chip electrophoresis, *Electrophoresis*, 24 (2003) 3476 - 3483.
- Kang, Y.J., Yang, C. and Huang, X.Y., Dynamic aspects of electroosmotic flow in a cylindrical microcapillary, *Int. J. Eng. Sci.*, 40 (2002a) 2203-2221.
- Kang, Y.J., Yang, C. and Huang, X.Y., Electroosmotic flow in a capillary annulus with high zeta potentials, *J. Colloid Interface Sci.*, 253 (2002b) 285-294.
- Keh, H.J. and Liu, Y.C., Electrokinetic flow in a circular capillary with a surface charge layer, *J. Colloid Interface Sci.*, 172 (1995) 222-229.
- Keh, H.J. and Tseng, H.C., Transient Electrokinetic flow in fine capillaries, *J. Colloid interface Sci.*, 242(2001) 450-459.

REFERENCES

- Kim, M.J., Beskok, A., and Kihm, K.D., Electro-osmosis-driven micro-channel flows: a comparative study of microscopic particle image velocimetry measurements and numerical simulations, *Experiments in Fluids*, 33 (2002) 170-180.
- Knox, J.H., Thermal effects and band spreading in capillary electro-separation. *Chromatographia*, 26 (1988) 329-337.
- Knox, J.H. and McCormack, K.A., Temperature effects in capillary electrophoresis 1: internal capillary temperature and effect upon performance, *Chromatographia*, 38 (1994a) 207-214.
- Knox, J.H. and McCormack, K.A., Temperature effects in capillary electrophoresis 2: Some theoretical calculations and predictions, *Chromatographia*, 38 (1994b) 215-221.
- Koh, W.H. and Anderson, J.L., Electroosmosis and electrolyte conductance in charged microcapillaries, *AIChE J.*, 21 (1975) 1176-1188.
- Kopp, M.U., De Mello, A.J., Manz, A, Chemical amplification: continuous-flow PCR on a chip, *Science*, 280 (1998) 1046-1048.
- Krylov, S.N., and Dovichi, N.J., Capillary Electrophoresis for the Analysis of Biopolymers, *Anal. Chem.*, 72 (2000) 111R-128R.
- Lacey, M.E., Webb, A.G., Sweedler, J.V., Monitoring temperature changes in capillary electrophoresis with nanoliter-volume NMR thermometry, *Anal. Chem.*, 72 (2000) 4991-4998.
- Lagally, E.T., Medintz, I, Mathies, R.A. Single-Molecule DNA Amplification and analysis in an integrated microfluidic device, *Anal Chem.*, 73 (2001) 565-570.
- Levine, S., Marriott, J.R., Neale, G. and Epstein, N., Theory of electrokinetic flow in fine cylindrical capillaries at high zeta potentials, *J. Colloid Interface Sci.*, 52 (1975) 136-149.
- Lin, H., Storey, B.D., Oddy, M.H., Chen, C.-H. and Santiago, J.G., Instability of electrokinetic microchannel flows with conductivity gradients, *Physics of fluids*, 16 (2004) 1922-1935.
- López-García, J.J., Horno, J., González-Caballero, F., Grosse, C. and Delgado, A.V., Dynamics of the electric double layer: analysis in the frequency and time domains, *J. Colloid Interface Sci.*, 228 (2000) 95-104.
- Lukkari, P., Jussila, M. and M.J. Riekkola, Home-made temperature control unit for the waters quanta 4000 capillary electrophoresis system, *J. High Resol. Chromatogr.*, 17 (1994) 651-654.

REFERENCES

- Mala, G.M., Li, D., Werner, C., Jacobasch, H.J. and Ning, Y.B., Flow characteristics of water through a microchannel between two parallel plates with electrokinetic effects, *Int. J. Heat and Fluid Flow*, 18 (1997a) 489-496.
- Mala, G.M., Li, D. and Dale, J.D., Heat transfer and fluid flow in microchannels, *Int. J. Heat Mass Transfer*, 40 (1997b) 3079-3088.
- Mao, H., Yang, T. and Cremer, P.S., A microfluidic device with a linear temperature gradient for parallel and combinatorial measurements, *J. Am. Chem. Soc.*, 124 (2002) 4432-4435.
- Marcos, Yang, C., Ooi, K.T., Wong, T.N. and Masliyah J.H., Frequency-dependent laminar electroosmotic flow in a closed-end rectangular microchannel, *J. Colloid Interface Sci.*, 275 (2004) 679-698.
- Masliyah, J.H. *Electrokinetic Transport Phenomena*. AOSTRA Technical Publication Series, No. 12, AOSTRA, Edmonton, 1994.
- Maynes D. and Webb B.W., Fully developed electro-osmotic heat transfer in microchannels *Int. J. Heat Mass Transfer* 46 (2003a) 1359-1369.
- Maynes D, and Webb B.W., Fully-developed thermal transport in combined pressure and electro-osmotically driven flow in microchannels, *ASME J. Heat Transfer*, 125 (2003b) 889-895.
- Maynes D. and Webb B.W., The effect of viscous dissipation in thermally fully-developed electro-osmotic heat transfer in microchannels, *Int. J. Heat Mass Transfer*, 47 (2004) 987-999.
- Meinhart, C.D., Wereley, S.T. and Santiago, J.G., *Micron-Resolution Velocimetry Techniques*, in: *Developments in Laser Techniques and Applications to Fluid Mechanics*, Adrian, R.J. *et al.* (Eds.), Springer-Verlag, Berlin, 1998.
- Minerick, A., Takhistov, P., Zhou, R., and Chang, H.-C., Manipulation and characterization of red blood cells with AC fields in micro-devices, *Electrophoresis*, 24 (2003), 3703-3717.
- Mitchell, M.J., Qiao, R. and Aluru, N.R., Meshless analysis of steady-state electroosmotic transport, *J. Microelectromechanical Sys.*, 9 (2000) 435-449.
- Northup, M.A., Hills, R.F., Landre, R., Lehew, H.D. and Watson, R.A., A MEMS-based DNA analysis system, *Transducers'95*, Eighth International Conference on Solid State Sensors and Actuators, Stockholm, Sweden, 764-767, June. 1995.
- Ng, A.S.W, Hau, W.L.W., Lee, Y.-K. and Zohar, Y., Electrokinetic generation of microvortex patterns in a microchannel liquid flow *J. Micromech. Microeng.* 14 (2004)

REFERENCES

247–255.

Oddy, M.H., Santiago, J.G. and Mikkelsen, J.C., Electrokinetic instability micromixing, *Anal. Chem.*, 73 (2001) 5822-5832.

Oddy, M.H. and Santiago, J.G., Multiple-species model for electrokinetic instability, *Physics of fluids*, 17 (2005) 1-17.

Ohara, T., Torii, D., Majumdar, A. and Dunphy, K., Transport of biomolecules in the ratcheting electrophoresis microchip (REM), The 6th ASME-JSME Thermal Engineering Joint Conference (2003), TED-AJ03-406.

Overbeek, J.Th.G., Phenomenology of Lyophobic, Chapter II In: H.R. Kruyt (Ed.), *Colloid Science*, Amsterdam, 1952.

Pamukcu, S., Electro-chemical technologies for in-situ restoration of contaminated subsurface soils, *EJGE*, 2 (1997) 1-10.

Patankar, N.A. and Hu, H.H., Numerical simulation of electroosmotic flow, *Anal. Chem.*, 70 (1998) 1870-1881.

Patankar, S.V., *Numerical Heat Transfer and Fluid Flow*, McGraw-Hill, New York, 1980.

Patankar, S.V., *Computation of conduction and duct flow heat transfer*. Innovative Research, Inc., 1991.

Paul, P.H., GarguiloM, G., and Rakestraw, D.J., Imaging of pressure- and electrokinetically driven flows through open capillaries, *Anal. Chem.*, 70 (1998), 2459–2467.

Peaceman, D and Rachford, H., The numerical solution of parabolic and elliptic equations, *J. Soc. Indust. Appl. Math.*, 3 (1955), 28-41

Peled, N., Design and implementation of a microchemistry analyzer, *Pure & Appl. Chem.*, **68** (1996), No. 10, 1837-1841.

Philip, J.R. and Wooding, R.A., Solution of the Poisson-Boltzmann equation about a cylindrical particle, *J. Chem. Phys.*, 52 (1970) 953-961.

Probstein, R.F., *Physicochemical Hydrodynamics: An Introduction*, 2nd ed., John Wiley & Sons, New York, 1994.

Qian, Y., Yang, G. and Bowen, W.R., An algorithm for the calculation of the electrical potential distribution in a charged capillary with general electrolytes, *J. Colloid Interface Sci.*, 190 (1997) 55-60.

REFERENCES

- Qian, Y. and Bowen, W.R., Accuracy assessment of numerical solutions of the nonlinear Poisson-Boltzmann equation for charged colloidal particles, *J. Colloid Interface Sci.*, 201(1998) 7-12.
- Qu, W. and Li, D., A model for overlapped EDL fields, *J. Colloid Interface Sci.*, 224 (2000) 397-407.
- Ramos, A., Morgan, H., Green, N.G. and Castellanos, A., AC electric field induced fluid flow in microelectrodes, *J. Colloid Interface Sci.*, 217 (1999) 420-422.
- Ren, L., Escobedo, C. and Li, D., Electroosmotic flow in a microcapillary with one solution displacing another solution, *J. Colloid Interface Sci.*, 242 (2001) 264-271.
- Ren, L., Escobedo, C. and Li, D., A new method of evaluating the average electro-osmotic velocity in microchannels, *J. Colloid Interface Sci.*, 250 (2002) 238-242.
- Ren, L. and Li, D., Electroosmotic flow in heterogeneous microchannels, *J. Colloid Interface Sci.*, 243 (2001) 255-261.
- Ren, L., Sinton, D. and Li, D., Numerical simulation of microfluidic injection processes in crossing microchannels, *J. Micromech. Microeng.* 13 (2003) 739-747.
- Ren, L., and Li, D., Electroviscous effects on pressure-driven flow of dilute electrolyte solutions in small microchannels. *J. Colloid and Interface Sci.*, 274 (2004) 319-330.
- Reuss, F.F., Sur un nouvel effet de l'électricité galvanique *Mémoires de la Société Impériale des Naturalistes de Moscou*, 2 (1809), 327– 337.
- Rice, C.L. and Whitehead, R., Electrokinetic flow in narrow cylindrical capillaries, *J. Phys. Chem.*, 69 (1965) 4017-4023.
- Ross, D., Johnson, T.J., and Locascio, L.E., Imaging of electroosmotic flow in plastic microchannels. *Anal. Chem.*, 73 (2001a) 2509-2515.
- Ross, D., Gaitan, M., and Locascio, L.E., Temperature measurement in microfluidic systems using a temperature-dependent fluorescent dye, *Anal. Chem.*, 73 (2001b) 4117-4123.
- Ross, D. and Locascio, L.E., Microfluidic temperature gradient focusing, *Anal. Chem.*, 74 (2002) 2556 – 2564.
- Sakakibara, J., and Adrian, R.J., Whole field measurement of temperature in water using two-color laser induced fluorescence, *Experiments in Fluids*, 26 (1999) 7-15.
- Samson, E. and Marchand, J., Numerical solution of the extended Nernst-Planck model, *J. Colloid Interface Sci.*, 215 (1999) 1-8.

REFERENCES

- Santiago, J.G., Electroosmotic flows in microchannels with finite inertial and pressure forces, *Anal. Chem.*, 73 (2001) 2353-2365.
- Seiler, K., Harrison, D.J., Manz, A., Planar glass chips for capillary electrophoresis: repetitive sample injection, quantitation, and separation efficiency, *Anal. Chem.*, 65(1993), 1481-1488.
- Shin, S.M., Kang, I.S. and Cho, Y.-K., Mixing enhancement by using electrokinetic instability under time-period electric field *J. Micromech. Microeng.* 15 (2005) 455-462.
- Sinton, D., Microscale flow visualization, *Microfluid Nanofluid*, 1 (2004) 2-21.
- Söderman, O. and Jönsson, B., Electro-osmosis: Velocity profiles in different geometries with both temporal and spatial resolution, *J. Chem. Phys.*, 105 (1996) 10300-10311.
- Swinney, K. and Bornhop, D.J., Quantification and evaluation of Joule heating in on-chip capillary electrophoresis, *Electrophoresis*, 23 (2002) 613-620.
- Takhistov, P., Duginova, K. and Chang, H.-C., Electrokinetic mixing vortices due to electrolyte depletion at microchannel junctions. *J. Colloid Interfacial Sci.*, 263(2003), 133-143.
- Tang, G.Y., Yang, C., Chai, C.K. and Gong, H.Q., Modeling of electroosmotic flow and capillary electrophoresis with the Joule heating effect: the Nernst-Planck equation versus the Boltzmann distribution, *Langmuir*, 19(2003), 10975-10984.
- Tang, G.Y., Yang, C., Chai, C.K. and Gong, H.Q., Joule heating effect on electroosmotic flow and mass species transport in a microcapillary, *Int. J. Heat Mass Transfer*, 47(2004a), 215-227.
- Tang, G.Y., Yang, C., Chai, C.K. and Gong, H.Q., Numerical analysis of the thermal effect on electroosmotic flow and electrokinetic mass transport in microchannels, *Analytica Chimica Acta*, 507 (2004b), 27-37.
- Tang, G.Y., Yang, C., Gong, H.Q., Chai, C.K. and Lam, Y.C., On Electrokinetic mass transport in a microchannel with Joule heating effect, *ASME Journal of Heat transfer*, 127(2005), 660-663.
- Tassel, P.R.V., Miras, D., Hagege, A., Leroy, M., Voegel, J.C. and Schaaf, P., Control of protein adsorption in capillary electrophoresis via an irreversibly bound protein coating, *J. Colloid Interface Sci.*, 183 (1996) 269-273.
- Terabe, S., Otsuka, K. and Ando, T., Electrokinetic chromatography with micellar solution and open-tubular capillary, *Anal. Chem.*, 57 (1985) 834-841.

REFERENCES

- Thamida, S. and Chang, H.-C., Nonlinear electrokinetic ejection and entrainment due to polarization at nearly insulated wedges, *Phys. Fluids*, 14 (2002), 4315-4328.
- Thormann, W., Zhang, C.-X., Caslavská, J., Gebauer, P., Mosher, R. A., Modeling of the impact of ionic strength on the electroosmotic flow in capillary electrophoresis with uniform and discontinuous buffer systems, *Anal. Chem.*, 70(1998), 549-562.
- Tsai, C.-H., Yang, R.-J., Tai, C.-H. and Fu, L.-M., Numerical simulation of electrokinetic injection techniques in capillary electrophoresis microchips, *Electrophoresis*, 26 (2005) 674-686.
- Tsao, H.K., Electroosmotic flow through an annulus, *J. Colloid Interface Sci.*, 225 (2000) 247-250.
- Van de Ven, T.G.M., *Colloidal hydrodynamics*, Academic Press, San Diego, 1989.
- Wang, A. and Fang, Y., Applications of capillary electrophoresis with electrochemical detection in pharmaceutical and biomedical analyses, *Electrophoresis*, 21 (2000), 1281–1290.
- Wang, Y., Lin, Q., and Mukherjee, T., A model for Joule heating-induced dispersion in microchip electrophoresis, *Lab on a Chip*, 4 (2004) 625-631.
- Weast, R., Astle, M.J. and Beyer, W.H., *CRC Handbook of chemistry and physics*, CRC Press Inc., Boca Raton, 1986.
- Werner, C., Körber, H., Zimmermann, R., Dukhin, S. and Jacobasch, H.J., Extended electrokinetic characterization of flat solid surfaces, *J. Colloid Interface Sci.*, 208 (1998) 329-346.
- Weiner O.D., Servant G., Welch N.D., Mitchison T.J., Sedat J.W., Bourne H.R. Spatial control of actin polymerization during neutrophil chemotaxis, *Nature Cell Biol.*, 1 (1999) 75 – 81.
- White, F.M., *Viscous Fluid Flow*, McGraw-Hill, New York, 1991.
- Xuan X. and Li D., Joule heating effects on peak broadening in capillary zone electrophoresis, *J. Micromech. Microeng.*, 14 (2004) 1171–1180.
- Xuan, X., Xu, B., Sinton, D., and Li, D., Electroosmotic flow with Joule heating effects, *Lab on a Chip*, 4 (2004) 230-236.
- Xuan, X., Sinton, D., and Li, D., Thermal end effects on electroosmotic flow in a capillary, *Int. J. Heat Mass Transfer*, 47 (2004) 3145-3157.
- Xuan X. and Li D., Band-broadening in capillary zone electrophoresis with axial temperature gradients, *Electrophoresis*. 26 (2005) 166–175.

REFERENCES

Xuan, X., and Li, D., Analytical study of Joule heating effects on electrokinetic transportation in capillary electrophoresis, *J. of Chromatography A*, 1064 (2005) 227-237.

Yanenko, N.N., *The Method of Fractional Steps*, Springer Verlag, New York, 1979.

Yang, C., Transport of liquid in rectangular microchannels by electroosmotic pumping, in: F.E.H. Tay (Eds.), *Microfluidics and BioMEMS Applications*, Kluwer Academic Publishers, Boston, 2002.

Yang, C. and Li, D., Electrokinetic effects on pressure-driven liquid flows in rectangular microchannels, *J. Colloid Interface Sci.*, 194 (1997) 95-107.

Yang, C. and Li, D., Analysis of electrokinetic effects on the liquid flow in rectangular microchannels, *Colloids Surfaces A: Physicochem. Eng. Aspects*, 143 (1998) 339-353.

Yang, C., Li, D. and Masliyah, J.H., Modeling forced liquid convection in rectangular microchannels with electrokinetic effects, *Int. J. Heat Mass Transfer*, 41 (1998) 4229-4249.

Yang, C. and Huang, X.Y., *Proceeding of the international MEMS workshop 2001*. 142 – 150, Singapore, 2001.

Yang, C., Ng, C.B. and Chan, V., Transient Analysis of Electroosmotic flow in a slit microchannel, *J. Colloid Interface Sci.*, 248 (2002) 524-527.

Yang, R.J., Fu, L.M. and Hwang, C.C., Electroosmotic entry flow in a microchannel, *J. Colloid Interface Sci.* 244 (2001a) 173-179.

Yang, R.J., Fu, L.M. and Lin, Y.C., Electroosmotic flow in microchannel, *J. Colloid Interface Sci.*, 239(2001b) 98-105.

Yeung, K.K.C. and Lucy, C.A., Suppression of electroosmotic flow and prevention of wall adsorption in capillary zone electrophoresis using zwitterionic surfactants, *Anal. Chem.*, 69 (1997) 3435-3441.

Zhao, T.S., and Liao, Q., Thermal effects on electroosmotic pumping of liquids in microchannels, *J. Micromech. Microeng.*, 12 (2002) 962-970.

Zhang, H.Y., Li, Q.F., Hu, Z.D., Wang, R. and Chen, X.G., Recalculation of the temperature inside capillaries using high buffer concentrations, *J. Chromatography*, 907 (2001) 353-356.

Zholkovskij, E.K., Masliyah, J.H. and Czarnecki, J, Electroosmotic dispersion in microchannels with a thin double layer *Anal. Chem.* 75 (2003) 901–909.

APPENDIX

APPENDIX A

BUOYANCY EFFECT

Generally, the buoyancy effect can be evaluated by using a dimensionless parameter, the Grashof number Gr . To obtain an indication of the relative magnitude of the buoyancy and forced convection effects, the Navier-Stokes equation with buoyancy effect and forced convection is expressed as

$$\rho \frac{D\vec{u}}{Dt} = -\nabla p + \nabla \cdot [\mu(T)\nabla\vec{u}] + \rho g \beta (T - T_f) \quad (\text{A-1})$$

Introducing the following non-dimensional parameters:

$$\vec{\bar{u}} = \frac{\vec{u}}{U_{ref}} \quad \bar{p} = \frac{p}{\rho U_{ref}^2} \quad \bar{t} = \frac{U_{ref} \cdot t}{R} \quad \bar{\mu} = \frac{\mu(T)}{\mu_{ref}} \quad \bar{T} = \frac{T - T_{ref}}{T_0 - T_{ref}} \quad (\text{A-2})$$

Then, the Navier-Stokes equation can be normalized as:

$$\frac{D\vec{\bar{u}}}{D\bar{t}} = -\nabla \bar{p} + \frac{1}{\text{Re}} \left\{ \nabla \cdot [\bar{\mu} \nabla \vec{\bar{u}}] \right\} + \frac{Gr}{\text{Re}^2} \bar{T} \quad (\text{A-3a})$$

$$Gr = \frac{\rho^2 g \beta R^3 (T_0 - T_{ref})}{\mu^2} \quad \text{Re} = \frac{U_{ref} R}{\mu_{ref}} \quad (\text{A-3b})$$

where β is the coefficient of expansion, $\bar{T}$ is the dimensionless temperature difference, g is the gravitational acceleration, R is the characteristic length, μ is the viscosity, and ρ is the density. A scaling analysis shows that the term on the left-hand side and the first two terms on the right-hand side of Eq. (A-3a) are of order $O(1)$. Also, $\bar{T}$ is of order $O(1)$. Consequently, the buoyancy effect can be strongly enough to influence the velocity, on which the temperature and the sample dispersion will depend, only if the coefficient of $\bar{T}$ (i.e. $\frac{Gr}{\text{Re}^2}$) is of order $O(1)$ or larger.

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Therefore, the ratio of the Grashof number to the square of the Reynold number gives a qualitative indication of the influence of the buoyancy on the forced convection, which in turn will affect the dispersion.

The Grashof number in most typical microfluidic systems is of order 10^{-3} , and the typical Reynolds numbers is of order $O(10^{-1})$. Therefore, the ratio of the Grashof number to the square of the Reynolds number (i.e. $\frac{Gr}{Re^2}$) is of order $O(10^{-1})$; this indicates the buoyancy effect can be neglected as compared to the forced convection in most typical microfluidic systems.

APPENDIX B GRID SYSTEMS

B.1 Collocated grid system

The grid where all the variables are located at the center of the control volumes (at the different grid points) is the so-called collocated grid. The use of a collocated grid can cause a problem for the calculation of the flow profile.

For example,

$$\frac{du}{dx} = 0 \quad (\text{B-1})$$

Integrating this equation over the control-volume (see Fig. B-1) results in

$$u_e - u_w = 0 \quad (\text{B-2})$$

Using the piecewise-linear (central difference) profile and taking midway location for the interfaces, we can show the next equation.

$$u_E - u_W = 0 \quad (\text{B-3})$$

The problem is that such equation requires equal velocities at alternating grid points. Fig. B-2 shows a one-dimensional velocity profile that fits Eq. (B-3) but is incorrect.

Equivalent problems arise with the pressure term appearing in the momentum equation. In the momentum equations, the pressure source terms need a special treatment. If the velocities are stored at the same locations as the scalar variables such as pressure, temperature etc, a highly non-uniform pressure field can behave like a uniform field in the discretized momentum equations. For example, as shown in Fig.B-1, if the pressures at interfaces e and w are obtained by linear interpolation in uniform grids, the pressure gradient term in the u -momentum equation is given by

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$$\frac{\partial P}{\partial x} = \frac{P_e - P_w}{\Delta x} = \frac{\left(\frac{P_E + P_P}{2}\right) - \left(\frac{P_W + P_P}{2}\right)}{\Delta x} = \frac{P_E - P_W}{2\Delta x} \quad (\text{B-4})$$

This means that the momentum equation would contain a pressure difference between two alternate grid points, not between adjacent ones. Hence, a non-uniform wavy pressure field would behave like a uniform field as indicted by Eq. (B-4). It can be seen from Fig. B-3 that the pressure drop is zero according to Eq. (B-4). This pressure field, of course, is not realistic.

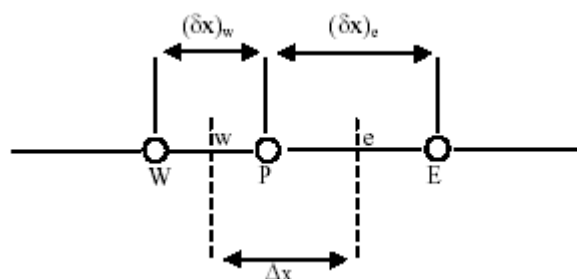


Fig. B-1 Grid-point cluster for a 1-D problem.

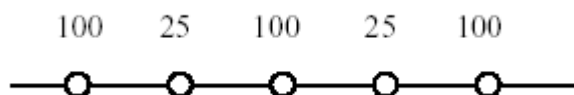


Fig. B-2 Incorrect velocity profile.

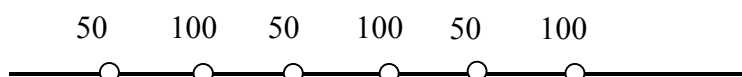


Fig. B-3 Wavy pressure field.

APPENDIX

B.2 Staggered grid system

A possible solution to such problem is to use a staggered grid system for the velocity components. In this method, the scalar variables, such as pressure, density, temperature etc are stored at ordinary grid points, while the velocity fields are stored at staggered grids which are centered around the control volume (CV) interfaces. The arrangement for a two-dimensional flow calculation is shown in Fig. B-4. The U -velocity is staggered in a half CV to the left. The V -velocity is staggered in a half CV downward. In the staggered grid arrangement, the pressure gradient term in the u -momentum equation is given by

$$\frac{\partial P}{\partial x} = \frac{P_P - P_W}{\delta x} \quad (\text{B-5})$$

Eq. (B-5) shows that the discretized pressure gradient only contains the difference of adjacent pressure components, and hence the above-mentioned problem is eliminated,

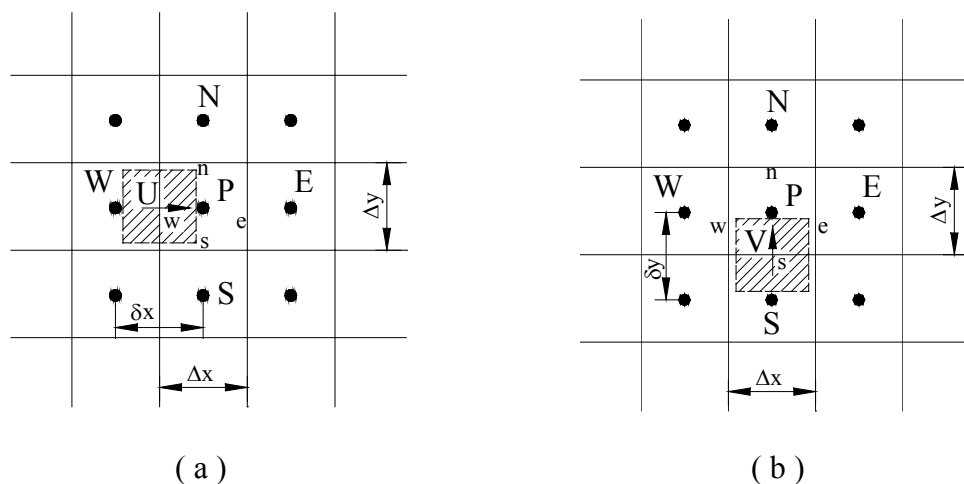


Fig. B-4 Diagram of staggered grid.

APPENDIX C

SIMPLER METHOD

The momentum equations are pressure-velocity coupling equations. The velocity fields can be solved using the iterative method if the pressure field is given or estimated. However, as mentioned earlier, there is no independent equation (e.g. the equation of state for compressible gases) for the pressure. Fortunately the continuity equation can be used to improve the estimated pressure. For convenience, Eq. (3-7) can be rewritten as

$$u_w = \hat{u}_w + (p_W - p_P)d_w \quad (\text{C-1})$$

where $\hat{u}_w = \frac{\sum a_{nb}u_{nb} + b}{a_w}$ and $d_w = \frac{A_w}{a_w}$.

The other velocity component v_s, w_b defined at the CV interfaces as shown in Fig. A-1 (b) can also be expressed using the same format as in Eq. (C-1).

Therefore, according to the CV defined in Fig. 3-1, the continuity equation can be discretized as

$$\begin{aligned} & \frac{\rho_P - \rho_P^0}{\Delta t} \Delta V + \\ & (\rho_e u_e - \rho_w u_w) \Delta y \Delta z + (\rho_n v_n - \rho_s v_s) \Delta z \Delta x + (\rho_t w_t - \rho_b w_b) \Delta x \Delta y = 0 \end{aligned} \quad (\text{C-1})$$

Substituting all the velocity components expressed by Eq. (C-1) into Eq. (C-2) gives

$$a_P p_P = a_E p_E + a_W p_W + a_N p_N + a_S p_S + a_T p_T + a_B p_B + b \quad (\text{C-3})$$

where

$$a_E = \rho_e d_e \Delta y \Delta z \quad (\text{C-4a})$$

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$$a_w = \rho_w d_w \Delta y \Delta z \quad (\text{C-4b})$$

$$a_n = \rho_n d_n \Delta x \Delta z \quad (\text{C-4c})$$

$$a_s = \rho_s d_s \Delta x \Delta z \quad (\text{C-4d})$$

$$a_t = \rho_t d_t \Delta y \Delta x \quad (\text{C-4e})$$

$$a_b = \rho_b d_b \Delta y \Delta x \quad (\text{C-4f})$$

$$a_p = a_E + a_w + a_n + a_s + a_t + a_b \quad (\text{C-4g})$$

$$b = \frac{\rho_P - \rho_P^0}{\Delta t} \Delta V + (\rho_w \hat{u}_w - \rho_e \hat{u}_e) \Delta y \Delta z + (\rho_s \hat{v}_s - \rho_n \hat{v}_n) \Delta x \Delta z + (\rho_b \hat{w}_b - \rho_t \hat{w}_t) \Delta x \Delta y \quad (\text{C-4h})$$

$$\Delta V = \Delta x \Delta y \Delta z \quad (\text{C-4i})$$

Eq. (C-3) can be used to improve the estimated pressure field. However, the velocity fields obtained by solving the momentum equations usually do not satisfy the continuity equation. As such, a velocity correction method is used, and the detail is outlined below.

In iterative processes, the velocities obtained by solving the momentum equations, and the pressure are taken as temporal values to which a small correction must be added

$$u = u^* + u' \quad p = p^* + p' \quad (\text{C-5})$$

In Eq. (C-5), u, p and u^*, p^* all satisfy the momentum equation Eq. (C-1).

Substituting Eq. (C-5) into Eq. (3-7) leads to

$$u'_w = \hat{u}'_w + (p'_w - p'_p) d_e \quad (\text{C-6})$$

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In SIMPLER algorithm, the $\hat{u}'$ is negligible.

Substituting Eq. (C-6) into Eq. (C-5) and dropping $\hat{u}'$ in Eq. (C-6) give a correction formula for u_w

$$u_w = u_w^* + (p'_w - p'_p)d_e \quad (C-7)$$

This formula can also be used to correct other velocity components defined at the CV interfaces. Applying these formulae to all velocity components and substituting them into Eq. (C-2), we can obtain

$$a_p p'_p = a_E p'_E + a_W p'_W + a_N p'_N + a_S p'_S + a_T p'_T + a_B p'_B + b \quad (C-8)$$

where $a_E, a_W, a_N, a_S, a_T, a_B$ and a_p are defined in Eqs. (C-4a)~(C-4f), and b is defined as

$$b = \frac{\rho_P - \rho_P^0}{\Delta t} \Delta V + (\rho_w u_w^* - \rho_e u_e^*) \Delta y \Delta z + (\rho_s u_s^* - \rho_n u_n^*) \Delta x \Delta z + (\rho_b u_b^* - \rho_t u_t^*) \Delta x \Delta y \quad (C-9)$$

Now, the SIMPLER algorithm can be described below:

- (1). Guess the initial velocity field;
- (2). Calculate the coefficients of Eq. (C-3) and obtain pressure field;
- (3). Use this pressure field to solve the momentum equations and obtain u^*, v^*, w^* ;
- (4). Solve Eq. (C-7) and Eq. (C-8) to obtain corrected velocities;
- (5). If necessary, solve the discretization equations for other $\Phi's$; and
- (6). Return to step 2 to repeat above steps until convergence is achieved.

APPENDIX D

SOLUTION OF LINEAR ALGEBRAIC EQUATIONS

In the previous sections, the convection-diffusion equations are discretized using the FVM. The resultant discretization is a system of algebraic equations, which are either linear or nonlinear, depending on the nature of the governing equations. No matter the equations are linear or not, efficient methods for solving linear systems of the algebraic equations are needed.

D.1 Tri-diagonal matrix algorithm (TDMA) method

For one-dimensional problems, the discretized algebraic equations usually have a simple structure. The corresponding coefficient matrix is a tridiagonal matrix. Only on the main diagonal and the diagonal immediately above and below it have nonzero terms. The algebraic equation can be expressed as

$$a_i \Phi_i = b_i \Phi_{i+1} + c_i \Phi_{i-1} + d_i \quad i = 2, 3, \dots, N-1 \quad (\text{D-1})$$

where Φ_1 and Φ_N are known as boundary values of the dependant values. The forward elimination and backward substitution can be used to solve this algebraic equation.

In the forward elimination, Φ_{i-1} is substituted by Φ_i ,

$$\Phi_{i-1} = P_{i-1} \Phi_i + Q_{i-1} \quad (\text{D-2})$$

Substituting Eq. (D-2) into Eq. (D-1) gives

$$\Phi_i = \frac{b_i}{a_i - c_i P_{i-1}} \Phi_{i+1} + \frac{c_i Q_{i-1} + d_i}{a_i - c_i P_{i-1}} \quad (\text{D-3})$$

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The backward substitution equation is

$$\Phi_i = P_i \Phi_{i+1} + Q_i \quad (\text{D-4})$$

where

$$P_i = \frac{b_i}{a_i - c_i P_{i-1}}, \quad Q_i = \frac{c_i Q_{i-1} + d_i}{a_i - c_i P_{i-1}} \quad (\text{D-5})$$

$$P_1 = \frac{b_1}{a_1} = 0, \quad Q_1 = \frac{d_1}{a_1} = \Phi_1 \quad (\text{D-6})$$

D.2 Line-by-line method

The line-by-line method can be used in two-dimensional or three-dimensional problems. For example, the discretized equation for general variable in two-dimension problems can be expressed as

$$a_P \Phi_P = a_E \Phi_E + a_W \Phi_W + (a_N \Phi_N + a_S \Phi_S + a_T \Phi_T + a_B \Phi_B + b) \quad (\text{D-7})$$

If the terms inside the brackets are known, this equation can be solved using the TDMA method. So, all the grid point values in a west-east line can be calculated using the following procedure: first, sweep from the south to the north in a plane, and then move to another plane, and repeat the same procedure until all the planes from the bottom to the top are scanned. Repeat these procedures until convergence is obtained. Alternating the sweep direction can accelerate the convergence, and hence the influence of all the boundary values is brought quickly into the interior of the calculation domain.

There are two kinds of iterations, inner iteration and outer iteration. The inner iteration refers to the solution of linear algebraic equations. In every inner iterative step, the coefficients are constant. The outer iteration refers to the solution of

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nonlinear problems. The coefficients and source terms must be updated after each outer iterative step is completed.

D.3 Alternating direction implicit (ADI) methods

The implicit matrix system resulted by the semi-implicit Crank-Nicolson scheme is too large for direct inversions and factorisation techniques. One way to overcome the difficulties is to use a splitting method. This method is known as the alternating direction implicit (ADI) method. The principle of the ADI method is to separate the operators into one-directional components and split the scheme into two (or three, for three-dimensional problems) steps, each one involving only the implicit operations originating from a single coordinate. This method has been introduced by *Peaceman and Rachford* (1955) and generalized by *Douglas and Gunn* (1964). Many developments and extensions have been brought to this approach by *Yanenko* (1979).

If the matrix operator Ω of Eq. (3-22) is separated into submatrices acting on the Φ components in a single direction, that is

$$\Omega = \Omega_x + \Omega_y + \Omega_z \quad (\text{D-8})$$

Then Eq. (3-22) becomes

$$\left[1 + \frac{\Delta t}{2}(\Omega_x + \Omega_y + \Omega_z)\right]\Phi^{t+1} = \left[1 - \frac{\Delta t}{2}(\Omega_x + \Omega_y + \Omega_z)\right]\Phi^t + \Delta t S^{t+1/2} \quad (\text{D-9})$$

The basic idea behind the ADI method consists of a factorization of the matrix operator in a product of one-dimensional operators, then Eq. (D-9) is factorized as follows:

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$$\begin{aligned}
& \left(1 + \frac{\Delta t}{2} \Omega_x\right) \left(1 + \frac{\Delta t}{2} \Omega_y\right) \left(1 + \frac{\Delta t}{2} \Omega_z\right) \Phi^{t+1} \\
& = \left(1 - \frac{\Delta t}{2} \Omega_x\right) \left(1 - \frac{\Delta t}{2} \Omega_y\right) \left(1 - \frac{\Delta t}{2} \Omega_z\right) \Phi^t + \Delta t S^{t+1/2}
\end{aligned} \tag{D-10}$$

Eq (D-10) represents an approximation to Eq. (3-18) of second-order accuracy, and it is equal to

$$\begin{aligned}
& \left[1 + \frac{\Delta t}{2} (\Omega_x + \Omega_y + \Omega_z)\right] \Phi^{t+1} = \left[1 - \frac{\Delta t}{2} (\Omega_x + \Omega_y + \Omega_z)\right] \Phi^t + \Delta t S^{t+1/2} \\
& + \frac{\Delta t^2}{4} (\Omega_x \Omega_y + \Omega_x \Omega_z + \Omega_y \Omega_z) (\Phi^{t+1} - \Phi^t) - \frac{\Delta t^3}{8} \Omega_x \Omega_y \Omega_z (\Phi^{t+1} + \Phi^t)
\end{aligned} \tag{D-11}$$

Since $(\Phi^{t+1} - \Phi^t)$ is of order Δt , the error terms are $O(\Delta t^3)$. Eq. (D-10) is then solved as a succession of one-dimensional Crank-Nicholson schemes:

$$\begin{aligned}
& \left(1 + \frac{\Delta t}{2} \Omega_x\right) \overline{\Phi^{t+1}} = \left(1 - \frac{\Delta t}{2} \Omega_x\right) \Phi^t + \Delta t S^{t+1/2} \\
& \left(1 + \frac{\Delta t}{2} \Omega_y\right) \overline{\overline{\Phi^{t+1}}} = \left(1 - \frac{\Delta t}{2} \Omega_y\right) \overline{\Phi^{t+1}} \\
& \left(1 + \frac{\Delta t}{2} \Omega_z\right) \Phi^{t+1} = \left(1 - \frac{\Delta t}{2} \Omega_z\right) \overline{\overline{\Phi^{t+1}}}
\end{aligned} \tag{D-12}$$

when the operators $\Omega_i (i = x, y, z)$ commute, we recover Eq. (D-10) by elimination of $\overline{\overline{\Phi^{t+1}}}$ and $\overline{\Phi^{t+1}}$. If the operators $\Omega_i (i = x, y, z)$ do not commute, approximation Eq. (D-12) is still valid, but is reduced to first order in time.

APPENDIX E

DIFFUSIVITY DUE TO TAYLOR-ARIS DISPERSION

As discussed in Chapter 5, for a fully developed electroosmotic flow without Joule heating effects $v = 0$ and $E_r = 0$. The mass transport equation (i.e. Eq. (5-17)) can be simplified to

$$\frac{\partial C_s}{\partial t} + (u + u_{ep}) \frac{\partial C_s}{\partial z} = D_{so} \frac{\partial^2 C_s}{\partial z^2} + \frac{D_{so}}{r} \frac{\partial}{\partial r} \left(r \frac{\partial C_s}{\partial r} \right) \quad (\text{E-1})$$

where based on Eq. (4-29), the dimensional EOF velocity is given by

$$u = -\frac{\varepsilon_0 \varepsilon_r E_z \zeta}{\mu} \left(1 - \frac{\psi}{\zeta} \right), \quad \text{and the electrophoretic velocity is expressed as}$$

$$u_{ep} = \mu_{ep0} E_z = \text{const}.$$

To obtain the analytical solution of Eq. (E-1), we apply the method of cross-sectional average, and then Eq. (E-1) is reduced to one-dimensional

$$\frac{\partial C^*}{\partial t} + (u^* + u_{ep}^*) \frac{\partial C^*}{\partial z} = D_{eff} \frac{\partial^2 C^*}{\partial z^2} \quad (\text{E-2})$$

where D_{eff} is the efficient mass diffusivity considering the real pure mass diffusion

(D_{so}) and the diffusion due to the Taylor-Aris dispersion (D_T), i.e. $D_{eff} = D_{so} + D_T$.

C^* , u^* and u_{ep}^* respectively refer to the cross-sectional averaged sample concentration, EOF velocity and electrophoretic velocity, and they are defined as

$$C^* = \frac{2}{R^2} \int_0^R C r dr \quad u_{ep}^* = \frac{2}{R^2} \int_0^R u_{ep} r dr = u_{ep} \quad u^* = \frac{2}{R^2} \int_0^R u r dr \quad (\text{E-3})$$

In order to evaluate the D_{eff} (i.e. D_T , since D_{so} is known), we set

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$$u = u^* + \Delta u \quad C = C^* + \Delta C \quad (\text{E-4a})$$

with the zero value for the cross-sectional averaged perturbation

$$(\Delta u)^* = \frac{2}{R^2} \int_0^R (\Delta u) r dr = 0 \quad (\Delta C)^* = \frac{2}{R^2} \int_0^R (\Delta C) r dr = 0 \quad (\text{E-4b})$$

where Δu and ΔC refer to the perturbation of the EOF velocity and sample species concentration, respectively.

Substituting equation (E-4a) into equation (E-1), we can show next

$$\begin{aligned} \frac{\partial C^*}{\partial t} + \frac{\partial(\Delta C)}{\partial t} + (u^* + u_{ep}) \frac{\partial C^*}{\partial z} + (\Delta u) \frac{\partial C^*}{\partial z} + (u^* + u_{ep}) \frac{\partial(\Delta C)}{\partial z} + \\ (\Delta u) \frac{\partial(\Delta C)}{\partial z} = D_{so} \frac{\partial^2 C^*}{\partial z^2} + D \frac{\partial^2(\Delta C)}{\partial z^2} + \frac{D_{so}}{r} \frac{\partial}{\partial r} \left[r \frac{\partial(\Delta C)}{\partial r} \right] \end{aligned} \quad (\text{E-5})$$

Carrying out the cross-sectional average of equation (E-1), we can obtain,

$$\frac{\partial C^*}{\partial t} + \left[(u + u_{ep}) \frac{\partial C}{\partial z} \right]^* = D_{so} \frac{\partial^2 C^*}{\partial z^2} \quad (\text{E-6})$$

Note that,

$$\begin{aligned} \left[(u + u_{ep}) \frac{\partial C}{\partial z} \right]^* &= \frac{\partial}{\partial z} [(u^* + u_{ep}) C^* + (\Delta u \Delta C)^*] = \\ (u^* + u_{ep}) \frac{\partial C^*}{\partial z} + \left[\Delta u \frac{\partial(\Delta C)}{\partial z} \right]^* \end{aligned} \quad (\text{E-7})$$

Hence equation (E-6) can be expressed as:

$$\frac{\partial C^*}{\partial t} + (u^* + u_{ep}) \frac{\partial C^*}{\partial z} = D \frac{\partial^2 C^*}{\partial z^2} - \left[\Delta u \frac{\partial(\Delta C)}{\partial z} \right]^* \quad (\text{E-8})$$

Combining equation (E-5) and equation (E-8) yields

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$$\begin{aligned}
& \frac{\partial(\Delta C)}{\partial t} + (\Delta u) \frac{\partial C^*}{\partial z} + (u^* + u_{ep}) \frac{\partial(\Delta C)}{\partial z} + (\Delta u) \frac{\partial(\Delta C)}{\partial z} \\
& = \frac{D}{r} \frac{\partial}{\partial r} \left[r \frac{\partial(\Delta C)}{\partial r} \right] + D \frac{\partial^2(\Delta C)}{\partial z^2} + \left[\Delta u \frac{\partial(\Delta C)}{\partial z} \right]^*
\end{aligned} \tag{E-9}$$

Relatively,

$$\begin{aligned}
\frac{\partial(\Delta C)}{\partial z} &<< \frac{\partial C^*}{\partial z} & \frac{\partial(\Delta C)}{\partial t} &\approx 0 & \frac{\partial^2(\Delta C)}{\partial z^2} &\approx 0 \\
\left[\Delta u \frac{\partial(\Delta C)}{\partial z} \right]^* &<< (\Delta u) \frac{\partial C^*}{\partial z}
\end{aligned} \tag{E-10}$$

Then equation (E-9) is simplified to

$$(\Delta u) \frac{\partial C^*}{\partial z} = \frac{D}{r} \frac{\partial}{\partial r} \left[r \frac{\partial(\Delta C)}{\partial r} \right] \tag{E-11}$$

Integrating equation (E-11) from 0 to r gives,

$$r \frac{\partial(\Delta C)}{\partial r} = \frac{1}{D} \frac{\partial C^*}{\partial z} \int_0^r \Delta u \, r dr \tag{E-12}$$

Further integrating equation (E-12) from 0 to r leads to

$$\Delta C(r, z) - \Delta C(0, z) = \frac{1}{D} \frac{\partial C^*}{\partial z} \int_0^r \frac{1}{r} \left(\int_0^r \Delta u \, r dr \right) dr \tag{E-13}$$

Differentiating equation (E-13) with respect to z gives

$$\frac{\partial \Delta C(r, z)}{\partial z} - \frac{\partial \Delta C(0, z)}{\partial z} = \frac{\partial^2 C^*}{\partial z^2} \frac{1}{D} \int_0^r \frac{1}{r} \left(\int_0^r \Delta u \, r dr \right) dr \tag{E-14}$$

Since $\frac{\partial \Delta C(0, z)}{\partial z}$ is independent of r , then

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$$\left[\Delta u \frac{\partial \Delta C(0, z)}{\partial z} \right]^* = (\Delta u)^* \frac{\partial \Delta C(0, z)}{\partial z} = 0 \quad (\text{E-15})$$

Therefore, according to equation (E-14), we have

$$\left(\Delta u \frac{\partial \Delta C}{\partial z} \right)^* = \frac{\partial^2 C^*}{\partial z^2} \frac{2}{DR^2} \int_0^R \Delta u \left[\int_0^r \frac{1}{r} \left(\int_0^r \Delta u r dr \right) dr \right] r dr = -D_T \frac{\partial^2 C^*}{\partial z^2} \quad (\text{E-16})$$

Hence, the induced diffusivity due to Taylor dispersion is expressed as

$$D_T = -\frac{2}{DR^2} \int_0^R \Delta u \left[\int_0^r \frac{1}{r} \left(\int_0^r \Delta u r dr \right) dr \right] r dr \quad (\text{E-17})$$

In order to evaluate D_T , we need to know Δu , which, according to equation (E-4b), is given by

$$\Delta u = u - u^* \quad (\text{E-18})$$

For electrokinetic flow in a steady state, fully-developed situation,

$$u = U_0 \left(1 - \frac{\psi}{\zeta} \right) \quad u^* = U_0 \left(1 - \frac{\psi^*}{\zeta} \right) \quad (\text{E-19})$$

Thus

$$\Delta u = U_0 \frac{\psi^* - \psi}{\zeta} \quad (\text{E-20})$$

In case of the Debye-Huckel linear approximation

$$\psi = \zeta \frac{I_0(\kappa r)}{I_0(\kappa R)} \quad \psi^* = \frac{2}{R^2} \int_0^r \psi r dr = \frac{2\zeta}{\kappa R} \frac{I_1(\kappa r)}{I_0(\kappa R)} \quad (\text{E-21})$$

Therefore,

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$$\Delta u = \frac{U_0}{I_0(\kappa R)} \left[\frac{2}{\kappa R} I_1(\kappa R) - I_0(\kappa r) \right] \quad (\text{E-22})$$

We can show the integration for

$$\begin{aligned} \int_0^r \Delta u r dr &= \frac{U_0}{I_0(\kappa R)} \int_0^r \left[\frac{2}{\kappa R} I_1(\kappa R) - I_0(\kappa r) \right] r dr = \\ &= \frac{U_0}{I_0(\kappa R)} \left[\frac{I_1(\kappa R)}{\kappa R} r^2 - \frac{I_0(\kappa r)}{\kappa} r \right] \end{aligned} \quad (\text{E-23})$$

$$\begin{aligned} \int_0^r \frac{1}{r} \left(\int_0^r \Delta u r dr \right) dr &= \frac{U_0}{I_0(\kappa R)} \int_0^r \left[\frac{I_1(\kappa R)}{\kappa R} r - \frac{I_0(\kappa r)}{\kappa} \right] dr \\ &= \frac{U_0}{I_0(\kappa R)} \left[\frac{I_1(\kappa R)}{2\kappa R} r^2 - \frac{I_0(\kappa r)}{\kappa^2} + \frac{1}{\kappa^2} \right] \end{aligned} \quad (\text{E-24})$$

Hence

$$\begin{aligned} &\int_0^R \Delta u \left[\int_0^r \frac{1}{r} \left(\int_0^r \Delta u r dr \right) dr \right] r dr \\ &= \frac{U_0^2}{I_0(\kappa R)^2} \int_0^R \left[\frac{2I_1(\kappa R)}{\kappa R} - I_0(\kappa r) \right] \left[\frac{I_1(\kappa R)}{2\kappa R} r^2 - \frac{I_0(\kappa r)}{\kappa^2} + \frac{1}{\kappa^2} \right] r dr \\ &= \frac{U_0^2}{I_0(\kappa R)^2} \left\{ \left[\frac{I_1(\kappa R)^2}{(\kappa R)^2} \frac{R^4}{4} \right] - \left[\frac{2I_1(\kappa R)}{\kappa^3 R} \frac{R}{\kappa} I_1(\kappa R) \right] + \left[\frac{2I_1(\kappa R)}{\kappa^3 R} \frac{1}{2} R^2 \right] \right. \\ &\quad \left. - \left[\frac{I_1(\kappa R)}{2\kappa R} \left(\frac{2R^2}{\kappa^2} I_2(\kappa R) + \frac{R^3}{\kappa} I_3(\kappa R) \right) \right] \right. \\ &\quad \left. + \left[\frac{1}{\kappa^2} \frac{R^2}{2} (I_0(\kappa R)^2 - I_1(\kappa R)^2) \right] - \left[\frac{1}{\kappa^2} \frac{R}{\kappa} I_1(\kappa R) \right] \right\} \\ &= \frac{U_0^2}{I_0(\kappa R)^2} \left[\left(-\frac{R^2}{4\kappa^2} - \frac{2}{\kappa^4} \right) I_1(\kappa R)^2 + \frac{R^2}{2\kappa^2} I_0(\kappa R)^2 \right. \\ &\quad \left. - \frac{R}{\kappa^3} I_1(\kappa R) I_2(\kappa R) - \frac{R^2}{2\kappa^2} I_1(\kappa R) I_3(\kappa R) \right] \end{aligned} \quad (\text{E-25})$$

Therefore

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$$\begin{aligned}
D_T &= -\frac{2}{DR^2} \int_0^R \Delta u \left[\int_0^r \frac{1}{r} \left(\int_0^r \Delta u r dr \right) dr \right] r dr \\
&= \frac{U_0^2}{D_{so}} \left[\left(\frac{1}{2\kappa^2} + \frac{4}{R^2 \kappa^4} \right) \frac{I_1(\kappa R)^2}{I_0(\kappa R)^2} - \frac{1}{\kappa^2} \right. \\
&\quad \left. + \frac{2}{\kappa^3 R} \frac{I_1(\kappa R) I_2(\kappa R)}{I_0(\kappa R)^2} + \frac{1}{\kappa^2} \frac{I_1(\kappa R) I_3(\kappa R)}{I_0(\kappa R)^2} \right]
\end{aligned} \tag{E-26}$$

where, I_2 is the first kind, second order modified Bessel function, and I_3 is the first kind, the third order modified Bessel function. Eq. (E-16) gives the approximation of the diffusivity due to Taylor-Aris dispersion.