



Micro- and Nanoscale Fluid Mechanics

Transport in Microfluidic Devices

BRIAN J. KIRBY



Micro- and Nanoscale Fluid Mechanics

TRANSPORT IN MICROFLUIDIC DEVICES

Brian J. Kirby

Cornell University



CAMBRIDGE
UNIVERSITY PRESS

CAMBRIDGE UNIVERSITY PRESS

Cambridge, New York, Melbourne, Madrid, Cape Town, Singapore,
São Paulo, Delhi, Dubai, Tokyo, Mexico City

Cambridge University Press

32 Avenue of the Americas, New York, NY 10013-2473, USA

www.cambridge.org

Information on this title: www.cambridge.org/9780521119030

© 2010 Brian J. Kirby

This publication is in copyright. Subject to statutory exception
and to the provisions of relevant collective licensing agreements,
no reproduction of any part may take place without the written
permission of Cambridge University Press.

First published 2010

Printed in the United States of America

A catalog record for this publication is available from the British Library.

Library of Congress Cataloging in Publication data

Kirby, Brian (Brian J.)

Micro- and nanoscale fluid mechanics : transport in microfluidic devices / Brian Kirby.

p. cm.

Includes bibliographical references and index.

ISBN 978-0-521-11903-0 (hardback)

1. Microfluidic devices. 2. Microfluidics. 3. Nanofluids. I. Title.

TJ853.4.M53K57 2010

620.1'064—dc22 2009053537

ISBN 978-0-521-11903-0 Hardback

Additional resources for this publication at www.cambridge.org/kirby

Cambridge University Press has no responsibility for the persistence or accuracy of
URLs for external or third-party Internet Web sites referred to in this publication and
does not guarantee that any content on such Web sites is, or will remain, accurate or
appropriate.

MICRO- AND NANOSCALE FLUID MECHANICS: TRANSPORT IN MICROFLUIDIC DEVICES

This text describes the physics of fluid transport in microfabricated and nanofabricated liquid-phase systems, with consideration of particles and macromolecules. This text brings together fluid mechanics, electrodynamics, and interface science with a focused goal of preparing the modern microfluidics researcher to analyze and model continuum fluid mechanical systems encountered when working with micro- and nanofabricated devices. This text is designed for classroom instruction and also serves as a useful reference for practicing researchers. Worked sample problems are inserted throughout to assist the student, and exercises are included at the end of each chapter to facilitate use in classes.

Brian J. Kirby currently directs the Micro/Nanofluidics Laboratory in the Sibley School of Mechanical and Aerospace Engineering at Cornell University. He joined the school in August 2004. Previously, he was a Senior Member of the Technical Staff in the Microfluidics Department at Sandia National Laboratories in Livermore, California. He was educated at Stanford University and The University of Michigan. Professor Kirby has received numerous research and teaching awards, including the Presidential Early Career Award for Scientists and Engineers (PECASE) and the Mr. and Mrs. Robert F. Tucker Excellence in Teaching Award.

Preface

This text focuses on the physics of liquid transport in micro- and nanofabricated systems. It evolved from a graduate course I have taught at Cornell University since 2005, titled “Physics of Micro- and Nanoscale Fluid Mechanics,” housed primarily in the Mechanical and Aerospace Engineering Department but attracting students from Physics, Applied Physics, Chemical Engineering, Materials Science, and Biological Engineering. This text was designed with the goal of bringing together several areas that are often taught separately – namely, fluid mechanics, electrodynamics, and interfacial chemistry and electrochemistry – with a focused goal of preparing the modern microfluidics researcher to analyze and model continuum fluid-mechanical systems encountered when working with micro- and nanofabricated devices. It omits many standard topics found in other texts – turbulent and transitional flows, rheology, transport in gel phase, Van der Waals forces, electrode kinetics, colloid stability, and electrode potentials are just a few of countless examples of fascinating and useful topics that are found in other texts, but are omitted here as they are not central to the fluid flows I wish to discuss.

Although I hope that this text may also serve as a useful reference for practicing researchers, it has been designed primarily for classroom instruction. It is thus occasionally repetitive and discursive (where others might state results succinctly and only once) when this is deemed useful for instruction. Worked sample problems are inserted throughout to assist the student, and exercises are included at the end of each chapter to facilitate use in classes. Solutions for qualified instructors are available from the publisher at <http://www.cambridge.org/kirby>. This text is *not* a summary of current research in the field and omits any discussion of microfabrication techniques or any attempt to summarize the technological state of the art.

The text considers, in turn, (a) low-Reynolds-number fluid mechanics and hydraulic circuits; (b) outer solutions for microscale flow, focusing primarily on the unique aspects of electroosmotic flow outside the electrical double layer; (c) inner solutions for microscale flow, focusing on sources of interfacial charge and modeling of electrical double layers; and (d) unsteady and nonequilibrium solutions, focusing on nonlinear electrokinetics, dynamics of electrical double layers, electrowetting, and related phenomena. In each case, several applications are selected to motivate the presentation, including microfluidic mixing, DNA and protein separations, microscale fluid velocity measurements, dielectrophoretic particle manipulation, electrokinetic pumps, and the like.

I select notation with the goal of helping students new to the field and with the understanding that this (on occasion) leads to redundant or unwieldy results. I minimize use of one symbol for multiple different variables, so the radius in spherical coordinates (r) is typeset with a symbol different from the radius in cylindrical coordinates (ρ) and the colatitudinal angle ϑ in spherical coordinates is distinguished from the polar coordinate in cylindrical coordinates (θ). Because I teach from this text using a chalkboard, I use symbols that I can reproduce on a chalkboard – thus I avoid the use of the Greek

letter ν for the kinematic viscosity $\nu = \eta/\rho$, because I am utterly unable to make it distinguishable from the y velocity v . Vectors, though they are placed in boldface to make them stand out, are also written with (admittedly redundant) superscripted arrows to match the chalkboard presentation.

This material is used for a semester-long graduate course at Cornell. Chapters 1, 2, 5, 7, and 8, as well as the appendices, are not covered in class as they are considered review or supplementary material. The remainder of the text is covered in approximately forty-two 50-minute classroom sessions.

I would like to acknowledge a number of people who helped with various aspects of this text. In particular, Dr. Elizabeth Strychalski and Professors Stephen Pope and Claude Cohen at Cornell, Professor Shelley Anna of Carnegie-Mellon University, Professor Kevin Dorfman of the University of Minnesota, Professor Nicolas Green of the University of Southampton, Donald Aubrecht of Harvard University, Professor Sumita Pennathur of UCSB, and Professor Aaron Wheeler of the University of Toronto were kind enough to offer useful suggestions. Professor Amy Herr of the University of California, Berkeley, used a draft of this text for her class during spring 2009; her insight and the feedback from her students were both immensely helpful. Professor Martin Bazant of the Massachusetts Institute of Technology provided materials helpful in completing the bibliography for several of the chapters. The students that have taken my class since 2004 have all contributed to this text in some way, but I would like to thank my student researchers Alex Barbati, Ben Hawkins, Sowmya Kondapalli, and Vishal Tandon in particular for their input, and my student Michael Allen for careful proofreading. Ben Hawkins and Dr. Jason Gleghorn contributed a number of the figures and helped to write material that was included in the chapters on Stokes flow and dielectrophoresis. David J. Griffiths (Reed College) provided files that assisted with typesetting. Gabe Terrizzi created many of the figures; his contributions were immensely helpful. Greg Parker (gparker@chorus.net) designed the cover.

Although many people assisted with review of this text, I am solely responsible for any errors, and I hope that readers will notify me or the publisher of those that they find. Errata will be maintained at <http://www.cambridge.org/kirby>.

Brian J. Kirby
Ithaca, NY
May 2010

Nomenclature

Symbol	Meaning	Page of first use or definition
A	area	61
\mathcal{A}	Helmholtz free energy	324
α	coefficient	112
α	phase lag angle	69
α	rotation angle	158
α	thermal diffusivity	80
a	acceleration	255
a	particle radius	171
a_i	activity	413
β	compressibility	75
β	coefficient	236
b	slip length	31
\vec{B}	applied magnetic field	391
\mathcal{B}	Brillouin function	104
c_i	species molar concentration	407
c_p	specific heat	80
c	passive scalar	80
C	capacitance	117
C	constant of integration	43
C_h	compliance	66
ζ	complex number	465
C_D	drag coefficient	188
Γ	2D vortex strength	163
Γ	circulation	13
Γ	surface chemical site density	229
Γ	magnitude of injected sample	90
γ	surface tension	20
γ_i	natural logarithm of species concentration	259
χ	electrokinetic coupling matrix	65
χ_e	electric susceptibility	100
χ_m	magnetic susceptibility	98
d	depth	140
d	diameter	22
D	scalar diffusivity	80
D_i	species diffusivity	252
\vec{D}	electric displacement	100

Symbol	Meaning	Page of first use or definition
Du	Dukhin number	263
δ	Dirac delta function	458
$\mathbf{\delta}$	identity tensor	16
∇	del operator	426
e	eccentricity	188
e	fundamental charge	201
e_1	singlet potential	475
e_2	pair potential	476
e_{mf}	potential of mean force	227
\vec{E}	electric field	97
ϵ	electrical permittivity	98
$\underline{\epsilon}$	complex electrical permittivity for sinusoidal fields	113
ϵ_S	Stern layer permittivity	360
ϵ_0	electrical permittivity of free space	100
ϵ_r	relative permittivity, i.e., dielectric constant	101
ϵ'	reactive permittivity	115
ϵ''	dissipative permittivity	115
ϵ_{LJ}	potential well depth	477
$\underline{\epsilon}$	strain rate tensor	10
$\frac{\partial \epsilon}{\partial c}$	dielectric increment	413
F	Faraday constant	99
\vec{F}	force	108
\vec{f}	force per unit volume	6
f_{CM}	Clausius–Mossotti factor	393
f_{ad}	adjusted distribution function	480
f_d	distribution function	217
f_{dc}	direct correlation function	482
f_{tc}	total correlation function	482
f_M	Mayer f function	480
f_0	Henry's function	288
f	electrophoretic correction factor	287
ϕ	electric potential	97
φ	electric potential difference from bulk	133
φ_0	total potential drop across the double layer	133
ϕ_v	velocity potential	153
$\underline{\phi}_v$	complex velocity potential	158
φ	azimuthal coordinate	419
Φ	cross-correlation	189
ζ	zeta potential	139
G	Gibbs free energy	20
G	electrical conductance	117
G_s	excess surface conductance	262
\vec{g}	gravitational acceleration	6
g_i	chemical potential	227
$\overline{g_i}$	electrochemical potential	227

Symbol	Meaning	Page of first use or definition
$\vec{\vec{G}}$	hydrodynamic interaction tensor	187
$\vec{\vec{G}}_0$	Oseen–Burgers tensor	187
H	capillary height	23
\vec{H}	induced magnetic field	98
h	height	43
η	dynamic viscosity	17
\vec{i}	current density	110
i_0	exchange current density	112
I	current	64
I	second moment of area	309
I_c	ionic strength	408
j	square root of minus 1	157
\vec{j}	scalar flux density	80
\mathcal{J}	Joukowski transform	171
k	spring constant	325
k	chemical reaction rate	409
k_{ve}	viscoelectric coefficient	235
k_B	Boltzmann constant	104
K_a	acid dissociation constant	409
K_{eq}	equilibrium constant	409
K_{sp}	solubility product	412
κ	2D doublet strength	165
κ	Debye screening parameter	288
Λ	molar conductivity	256
Λ	2D source strength	160
λ_B	Bjerrum length	478
λ_D	Debye length	202
λ_{HS}	hard-sphere packing length	213
λ_S	Stern layer thickness	360
ℓ_c	polymer contour length	301
ℓ_e	polymer end-to-end length	303
ℓ_K	polymer Kuhn length	312
ℓ_p	polymer persistence length	299
L	length	61
L	electrical inductance	117
L	depolarization factor	384
m	mass	184
\vec{M}	magnetization	98
μ	viscous mobility	252
μ_{DEP}	dielectrophoretic mobility	374
μ_{EK}	electrokinetic mobility	265
μ_{EO}	electroosmotic mobility	138
μ_{EP}	electrophoretic mobility	252
μ_{mag}	magnetic permeability	98
$\mu_{mag,0}$	magnetic permeability of free space	98
N_A	Avogadro's number	112

Symbol	Meaning	Page of first use or definition
N_{bp}	number of base pairs in DNA molecule	301
n	normal coordinate	106
p	pressure	6
\vec{p}	dipole moment	104
pK_a	negative logarithm of acid dissociation constant	410
pH	negative logarithm of molar proton concentration	410
pOH	negative logarithm of molar hydroxyl ion concentration	411
pzc	point of zero charge	230
\mathcal{P}	perimeter	63
\mathcal{P}	probability density function	313
Pe	mass transfer Peclet number	79
ϖ	dummy frequency integration variable	115
ψ	stream function	8
ψ_S	Stokes stream function	9
ψ_e	electric stream function	469
\vec{P}	electric polarization	100
\vec{P}	pressure interaction tensor	187
Q	volumetric flow rate	60
q	electric charge	97
q''	electric areal charge density	359
ρ	fluid density	6
ρ_E	net charge density	99
r	radial coordinate – spherical coordinates	418
r_h	hydraulic radius	63
Δr	radial distance – spherical coordinates	98
$\vec{\Delta r}$	distance vector	98
\mathcal{r}	radial coordinate – cylindrical coordinates	418
$\Delta \mathcal{r}$	radial distance – cylindrical coordinates	157
Re	Reynolds number	442
R	universal gas constant	112
R	electrical resistance	117
R	radius of channel	47
R	radius of curvature	21
R	separation resolution	267
R_h	hydraulic resistance	61
$\langle r_g \rangle$	radius of gyration	303
s	arc length	302
S	entropy	324
\mathcal{S}	Schwarz–Christoffel transform	473
σ	conductivity	110
σ_{LJ}	Lennard–Jones “bond length”	477
\mathfrak{g}	complex electrical conductivity	114
σ_s	effective surface conductivity	210

Symbol	Meaning	Page of first use or definition
Sk	Stokes number	186
St	Strouhal number	442
t	time	7
T	Kelvin temperature	20
\vec{T}	torque	109
$\vec{\bar{T}}$	Maxwell stress tensor	107
$\vec{\tau}$	stress tensor	15
τ	characteristic time	103
θ	polar coordinate – cylindrical coordinates	418
θ	contact angle	21
θ_0	corner angle	170
ϑ	colatitude coordinate – spherical coordinates	418
$\Delta\theta$	polar coordinate of distance vector	157
\vec{u}	velocity vector	7
\underline{u}	complex velocity	159
u_{EK}	electrokinetic velocity	269
u_{EO}	electroosmotic velocity	140
u_{EP}	electrophoretic velocity	255
u_z	radial velocity – cylindrical coordinates	8
u_r	radial velocity – spherical coordinates	9
u_θ	circumferential velocity – cylindrical coordinates	8
u_ϑ	circumferential velocity – spherical coordinates	9
\mathcal{U}	molecular internal energy	324
V	voltage	106
\mathcal{V}	volume	66
ω	angular frequency	49
$\vec{\omega}$	vorticity	12
$\vec{\bar{\omega}}$	rotation rate tensor	11
w	width	90
x	x coordinate	418
ξ	hard-sphere packing parameter	215
ξ	thermodynamic efficiency	143
y	y coordinate	418
Y	Young's modulus	309
z	z coordinate	418
z	valence magnitude for symmetric electrolytes	203
z_i	species valence	99
Z	partition function	326
\tilde{Z}	impedance	119
\tilde{Z}_b	hydraulic impedance	69

Subscript	Example	Meaning
0	p_0	phasor or sinusoid magnitude
0	w_0	value at reference state
∞	$c_{i,\infty}$	value in freestream or in bulk
bend	u_{bend}	bending
conv	$\bar{\mathbf{j}}_{\text{conv},i}$	convective
diff	$\bar{\mathbf{j}}_{\text{diff},i}$	diffusive
edl	q''_{edl}	electrical double layer
eff	ζ_{eff}	effective
ext	$\bar{\mathbf{E}}_{\text{ext}}$	extrinsic
H	u_H	high
L	u_L	low
m	ξ_m	suspending medium
n	E_n	normal
p	ρ_p	particle
pre	$\bar{\bar{\tau}}_{\text{pre}}$	isotropic (pressure) components
str	I_{str}	streaming
t	u_t	tangential
visc	$\bar{\bar{\tau}}_{\text{visc}}$	deviatoric (viscous) components
w	ρ_w	water

Superscript, accent	Example(s)	Meaning
$^\circ$	g_i°	value at reference condition
'	ϕ', y'	dummy integration variable
'	F', I'	per unit length
"	F'', q''	per unit area
', "	f', f''	derivatives of functions
'	ε'	reactive component
"	ε''	dissipative component
—	\bar{u}	spatially averaged
\sim	\underline{Z}	analytic representation of real parameters
$\vec{}$	\vec{u}, \vec{T}	vector or pseudovector
$\bar{\bar{}}$	$\bar{\bar{\tau}}, \bar{\bar{\varepsilon}}$	rank 2 tensor
$\hat{}$	$\hat{x}, \hat{\theta}$	unit vector
\wedge	\hat{e}_1	molar value
*	d^*, p^*	nondimensionalized quantity
$\langle \rangle$	$\langle \ell_e \rangle, \langle r_g \rangle$	time- or ensemble-averaged property
Δ	$\Delta p, \Delta x$	difference in property

Contents

<i>Preface</i>	page xv
<i>Nomenclature</i>	xvii
Introduction	1
1 Kinematics, Conservation Equations, and Boundary Conditions for Incompressible Flow	6
1.1 Fluid statics	6
1.2 Kinematics of a fluid velocity field	7
1.2.1 Important geometric definitions	7
1.2.2 Strain rate and rotation rate tensors	10
1.3 Governing equations for incompressible flow	13
1.3.1 Conservation of mass: continuity equation	13
1.3.2 Conservation of momentum: the Navier–Stokes equations	14
1.4 Constitutive relations	17
1.4.1 Relation between strain rate and stress	17
1.4.2 Non-Newtonian fluids	19
1.5 Surface tension	20
1.5.1 Definition of surface tension and interfacial energy	20
1.5.2 Young–Laplace equation	20
1.5.3 Contact angle	21
1.5.4 Capillary height	22
1.5.5 Dynamic contact angle	24
1.6 Velocity and stress boundary conditions at interfaces	24
1.6.1 Kinematic boundary condition for continuity of normal velocity	24
1.6.2 Dynamic boundary condition for continuity of tangential velocity	25
1.6.3 Dynamic boundary conditions for stresses	26
1.6.4 The physics of the tangential velocity boundary condition	30
1.7 Solving the governing equations	32
1.8 Flow regimes	33
1.9 A word on terminology and the microfluidics literature	33
1.10 Summary	34
1.11 Supplementary reading	36
1.12 Exercises	36
2 Unidirectional Flow	41
2.1 Steady pressure- and boundary-driven flow through long channels	41
2.1.1 Couette flow	41
2.1.2 Poiseuille flow	46

2.2	Startup and development of unidirectional flows	49
2.3	Summary	50
2.4	Supplementary reading	51
2.5	Exercises	51
3	Hydraulic Circuit Analysis	60
3.1	Hydraulic circuit analysis	60
3.2	Hydraulic circuit equivalents for fluid flow in microchannels	62
3.2.1	Analytic representation of sinusoidal pressures and flow rates	68
3.2.2	Hydraulic impedance	69
3.2.3	Hydraulic circuit relations	70
3.2.4	Series and parallel component rules	70
3.3	Solution techniques	72
3.4	Summary	74
3.5	Supplementary reading	75
3.6	Exercises	75
4	Passive Scalar Transport: Dispersion, Patterning, and Mixing	79
4.1	Passive scalar transport equation	80
4.1.1	Scalar fluxes and constitutive properties	80
4.1.2	Scalar conservation equation	80
4.2	Physics of mixing	82
4.3	Measuring and quantifying mixing and related parameters	84
4.4	The low-Reynolds-number, high-Peclet-number limit	87
4.4.1	The high-Peclet-number limit	87
4.4.2	The low-Reynolds-number limit	87
4.5	Laminar flow patterning in microdevices	88
4.6	Taylor–Aris dispersion	89
4.7	Summary	91
4.8	Supplementary reading	92
4.9	Exercises	92
5	Electrostatics and Electrodynamics	97
5.1	Electrostatics in matter	97
5.1.1	Electrical potential and electric field	97
5.1.2	Coulomb’s law, Gauss’s law for electricity in a material, curl of electric field	98
5.1.3	Polarization of matter and electric permittivity	100
5.1.4	Material, frequency, and electric-field dependence of electrical permittivity	102
5.1.5	Poisson and Laplace equations	104
5.1.6	Classification of material types	105
5.1.7	Electrostatic boundary conditions	105
5.1.8	Solution of electrostatic equations	107
5.1.9	Maxwell stress tensor	107
5.1.10	Effects of electrostatic fields on multipoles	108
5.2	Electrodynamics	109
5.2.1	Charge conservation equation	110
5.2.2	Electrodynamic boundary conditions	110
5.2.3	Field lines at substrate walls	112

5.3	Analytic representations of electrodynamic quantities: complex permittivity and conductivity	112
5.3.1	Complex description of dielectric loss	115
5.4	Electrical circuits	116
5.4.1	Components and properties	117
5.4.2	Electrical impedance	119
5.4.3	Circuit relations	119
5.4.4	Series and parallel component rules	120
5.5	Equivalent circuits for current in electrolyte-filled microchannels	122
5.5.1	Electrical circuit equivalents of hydraulic components	122
5.6	Summary	126
5.7	Supplementary reading	127
5.8	Exercises	127
6	Electroosmosis	131
6.1	Matched asymptotics in electroosmotic flow	132
6.2	Integral analysis of Coulomb forces on the EDL	132
6.3	Solving the Navier–Stokes equations for electroosmotic flow in the thin-EDL limit	135
6.3.1	Outer solution	136
6.3.2	Replacing the EDL with an effective slip boundary condition	136
6.3.3	Replacing the Navier–Stokes equations with the Laplace equation: flow–current similitude	137
6.3.4	Reconciling the no-slip condition with irrotational flow	138
6.4	Electroosmotic mobility and the electrokinetic potential	138
6.4.1	Electrokinetic coupling matrix representation of electroosmosis	140
6.5	Electrokinetic pumps	140
6.5.1	A planar electrokinetic pump	140
6.5.2	Types of electrokinetic pumps	143
6.6	Summary	145
6.7	Supplementary reading	145
6.8	Exercises	146
7	Potential Fluid Flow	153
7.1	Approach for finding potential flow solutions to the Navier–Stokes equations	153
7.2	Laplace equation for velocity potential and stream function	154
7.2.1	Laplace equation for the velocity potential	154
7.2.2	No-slip condition	156
7.3	Potential flows with plane symmetry	156
7.3.1	Complex algebra and its use in plane-symmetric potential flow	157
7.3.2	Monopolar flow: plane-symmetric (line) source with volume outflow per unit depth Λ	160
7.3.3	Plane-symmetric vortex with counterclockwise circulation per unit depth Γ	163
7.3.4	Dipolar flow: plane-symmetric doublet with dipole moment κ	165
7.3.5	Uniform flow with speed U	168
7.3.6	Flow around a corner	170
7.3.7	Flow over a circular cylinder	171
7.3.8	Conformal mapping	171

7.4	Potential flow in axisymmetric systems in spherical coordinates	172
7.5	Summary	173
7.6	Supplementary reading	173
7.7	Exercises	174
8	Stokes Flow	178
8.1	Stokes flow equation	178
8.1.1	Different forms of the Stokes flow equations	179
8.1.2	Analytical versus numerical solutions of the Stokes flow equations	180
8.2	Bounded Stokes flows	180
8.2.1	Hele-Shaw flows	181
8.2.2	Numerical solution of general bounded Stokes flow problems	182
8.3	Unbounded Stokes flows	182
8.3.1	Stokes flow over a sphere in an infinite domain	182
8.3.2	General solution for Stokes flow over a sphere in an infinite domain	187
8.3.3	Flow over prolate ellipsoids	188
8.3.4	Stokes flow over particles in finite domains	189
8.3.5	Stokes flow over multiple particles	189
8.4	Micro-PIV	189
8.4.1	Deterministic particle lag	191
8.4.2	Brownian motion	191
8.5	Summary	191
8.6	Supplementary reading	192
8.7	Exercises	193
9	The Diffuse Structure of the Electrical Double Layer	199
9.1	The Gouy–Chapman EDL	199
9.1.1	Boltzmann statistics for ideal solutions of ions	200
9.1.2	Ion distributions and potential: Boltzmann relation	201
9.1.3	Ion distributions and potential: Poisson–Boltzmann equation	202
9.1.4	Simplified forms of the nonlinear Poisson–Boltzmann equation	203
9.1.5	Solutions of the Poisson–Boltzmann equation	204
9.2	Fluid flow in the Gouy–Chapman EDL	208
9.3	Convective surface conductivity	210
9.4	Accuracy of the ideal-solution and Debye–Hückel approximations	211
9.4.1	Debye–Hückel approximation	212
9.4.2	Limitations of the ideal solution approximation	213
9.5	Modified Poisson–Boltzmann equations	213
9.5.1	Steric correction to ideal solution statistics	213
9.5.2	Modified Poisson–Boltzmann equation	215
9.5.3	Importance and limitations of Poisson–Boltzmann modifications	216
9.6	Stern layer	217
9.7	Summary	217
9.8	Supplementary reading	218
9.9	Exercises	218
10	Zeta Potential in Microchannels	225
10.1	Definitions and notation	225
10.2	Chemical and physical origins of equilibrium interfacial charge	226
10.2.1	Electrochemical potentials	226

10.2.2	Potential-determining ions	227
10.2.3	Nernstian and non-Nernstian surfaces	230
10.3	Expressions relating the surface charge density, surface potential, and zeta potential	232
10.3.1	Extended interface models: modifications to φ_0	234
10.3.2	Fluid inhomogeneity models: relation between φ_0 and ζ	234
10.3.3	Slip and multiphase interface models: hydrophobic surfaces	236
10.4	Observed electrokinetic potentials on microfluidic substrates	237
10.4.1	Electrolyte concentration	237
10.4.2	pH dependence	238
10.5	Modifying the zeta potential	238
10.5.1	Indifferent electrolyte concentrations	238
10.5.2	Surface-active agents	239
10.5.3	Chemical functionalizations	240
10.6	Chemical and fluid-mechanical techniques for measuring interfacial properties	240
10.6.1	Charge titration	240
10.6.2	Electroosmotic flow	241
10.6.3	Streaming current and potential	242
10.7	Summary	245
10.8	Supplementary reading	246
10.9	Exercises	247
11	Species and Charge Transport	250
11.1	Modes of species transport	250
11.1.1	Species diffusion	250
11.1.2	Convection	250
11.1.3	Relating diffusivity and electrophoretic mobility: the viscous mobility	252
11.2	Conservation of species: Nernst–Planck equations	253
11.2.1	Species fluxes and constitutive properties	253
11.2.2	Nernst–Planck equations	254
11.3	Conservation of charge	256
11.3.1	Charge conservation equation	256
11.3.2	Diffusivity, electrophoretic mobility, and molar conductivity	258
11.4	Logarithmic transform of the Nernst–Planck equations	258
11.5	Microfluidic application: scalar-image velocimetry	259
11.5.1	SIV using caged-dye imaging	259
11.5.2	SIV using photobleaching	259
11.6	Summary	259
11.7	Supplementary reading	261
11.8	Exercises	261
12	Microchip Chemical Separations	265
12.1	Microchip separations: experimental realization	265
12.1.1	Sample injection	266
12.1.2	Resolution	267
12.2	1D Band broadening	268
12.2.1	Analyte transport: quiescent flow, no electric field	268
12.2.2	Transport of analytes: electroosmotic flow and electrophoresis	269