A STUDY OF ELECTROCHEMICAL TRANSPORT AND DIFFUSE CHARGE DYNAMICS IN NANOSCALE DEVICES USING A LANGEVIN EQUATION

BY

DA KU

THESIS

Submitted in partial fulfillment of the requirements for the degree of Master of Science in Mechanical Engineering in the Graduate College of the University of Illinois at Urbana-Champaign, 2013

Urbana, Illinois

Adviser:

Assistant Professor David Saintillan
ABSTRACT

This thesis aims to develop new numerical and computational tools to study electrochemical transport and diffuse charge dynamics at small scales. Previous efforts at modeling electrokinetic phenomena at scales where non-continuum effects become significant have included continuum models based on the Poisson-Nernst-Planck equations and atomic simulations using molecular dynamics algorithms. Neither of them is easy to use or conducive to electrokinetic transport modeling in strong confinement or over long time scales. This work introduces a new approach based on a Langevin equation for diffuse charge dynamics in nanofluidic devices, which incorporates features from both continuum and atomistic methods. The model is then extended to include steric effects resulting from finite ion size, and applied to various phenomena involving charge dynamics between parallel-plate blocking electrodes. An efficient $N \log N$ algorithm for Stokes suspension simulations in doubly-periodic confined geometries is also developed, and applied to simulate electro-osmosis. Finally, the results of this approach are compared to those of the continuum model based on the Poisson-Nernst-Planck and Stokes equations.
To my parents, for their love and support.
ACKNOWLEDGMENTS

The author wishes to express sincere appreciation and gratitude towards Professor Saintillan for his guidance over the period of this study. His support and patience have been invaluable. The author also thanks his parents for their constant encouragement and support. Finally, he wishes to acknowledge the academic resources made available by the University of Illinois, in particular the Grainger Engineering Library for access to instructional materials on this interesting but initially unfamiliar subject.
# TABLE OF CONTENTS

CHAPTER 1 INTRODUCTION ........................................... 1  
\hspace{1em} 1.1 Background ........................................ 3  
\hspace{1em} 1.2 Overview ......................................... 5  

CHAPTER 2 THEORY .................................................. 6  
\hspace{1em} 2.1 The Continuum Approach .............................. 6  
\hspace{1em} 2.2 The Langevin Approach .............................. 9  
\hspace{1em} 2.3 Multi Diffusivity and Multi Valence ............... 11  
\hspace{1em} 2.4 Electro-Osmotic Flow ............................... 13  

CHAPTER 3 METHODS ............................................... 15  
\hspace{1em} 3.1 Using FFT to Solve Poisson’s Equation ............ 15  
\hspace{1em} 3.2 SPME (Smooth Particle Mesh Ewald) Approach .... 17  
\hspace{1em} 3.3 Stokes Interactions ................................. 21  
\hspace{1em} 3.4 Improved Convergence of the “Boundary Correction” Method with Image System .......................... 26  
\hspace{1em} 3.5 Steric Interactions .................................. 31  

CHAPTER 4 RESULTS AND DISCUSSION .............................. 35  
\hspace{1em} 4.1 Confined Stokes Flow Field ......................... 36  
\hspace{1em} 4.2 Convergence ........................................... 45  
\hspace{1em} 4.3 Steady State Charge Density ......................... 51  
\hspace{1em} 4.4 Transient of Charge Density ......................... 53  
\hspace{1em} 4.5 Simulating Electro-Osmotic Flow .................... 56  

CHAPTER 5 CONCLUSION, APPLICATION AND FUTURE WORK ........................................... 58  
\hspace{1em} 5.1 Summary and Conclusion ............................ 58  
\hspace{1em} 5.2 Potential Applications ............................... 59  
\hspace{1em} 5.3 Future Work .......................................... 61  

APPENDIX A EWALD SUM FORMULATION ......................... 63  
\hspace{1em} A.1 Periodic Stokes Equation ......................... 63  
\hspace{1em} A.2 Point Force ....................................... 64  
\hspace{1em} A.3 Force Dipole ...................................... 67  
\hspace{1em} A.4 Mass Dipole ..................................... 69
APPENDIX B  THE “BOUNDARY CORRECTION” METHOD
FORMULATION ............................................. 72
B.1  Arbitrary Boundary Condition (2 walls are different) .... 72
B.2  Periodic Boundary Condition in z (2 walls are the same) ... 75

APPENDIX C  DERIVATION OF GREEN’S FUNCTION FOR
2D PERIODIC STOKES FLOW ............................. 76
C.1  2D Periodic Stokes Equation ............................ 76
C.2  z force .................................................. 77
C.3  x force .................................................. 78

APPENDIX D  NONDIMENSIONALIZATION FOR MULTI SPECIES
EQUATIONS ................................................ 81
D.1  Dimensionless Variables ................................ 81
D.2  Scaling of the One-Dimensional PNP Equations .......... 82
D.3  Scaling of Langevin Equation ............................ 83

REFERENCES .............................................. 84
CHAPTER 1
INTRODUCTION

Recent advances in microfabrication technologies have enabled engineers and scientists to design and manufacture ever smaller fluidic devices to meet new engineering challenges and tackle new applications [1, 2, 3]. These new breakthroughs in manufacturing, akin to the advent of micro-fabricated integrated circuits a few decades earlier, have generated much interest over the last few years owing to their potential applications in a variety of fields and specifically for the miniaturization of chemical and biological assays [4, 5, 6]. Yet more recently, efforts have focused on further scaling these devices down to the nanoscale, opening a new realm of physical phenomena [7]. The emergence of micro and nanofluidics and of lab-on-chip technology has enabled the development of numerous novel devices achieving various functions, among which for instance: cell separation and sorting [8], micro and nano-bubble and capsule generation [9, 10, 11, 12], chemical and biochemical separations [13], biochemical detection and analysis [14], logic gates [15, 16], and many others.

Concomitantly, these developments have brought about a wealth of new design and modeling challenges, as the physics that govern these systems differ significantly from their macroscale counterparts [1]. In particular, fluid flows in micro and nanodevices are characterized by the complete absence of inertia, which makes them reversible and renders mixing difficult. In addition, they are often dominated by interfacial effects owing to the large surface-to-volume ratio at these length scales. Thermal, electric and chemical effects are also often present and intimately coupled, leading to a broad spectrum of new phenomena for which a good theoretical understanding and accurate models are often lacking.

Of particular interest has been the use of electric fields and electrokinetic phenomena in these devices as an efficient and low-cost means for transporting fluid and manipulating particles [17] or macromolecules [18]. Most solid
surfaces possess a native charge resulting from chemical reactions with the surrounding electrolyte [17, 19, 20]. These charged surfaces in turn attract ions of opposite charge in the liquid, which accumulate near the boundary creating an electrical double layer. When subjected to an electric field, this double layer exerts a body force on the fluid near the surface, which can drive fluid or particle motion. This technique for manipulating fluid and particles is especially useful in small devices and typically preferred to pressure-driven flow owing to its low cost and high efficiency as well as its ability to reduce particle or solute dispersion.

A number of recently developed technological applications utilize electrokinetic phenomena as a way to either transport fluid or particles or macromolecules. Some of these applications include: separation of DNA oligonucleotides by electrophoresis in straight nanochannels [13]; water analysis and treatment using electro-osmosis through nanocapillary array membranes [7, 21, 22, 23]; electrohydrodynamic stretching of long-chain DNA molecules [24, 25]; translocation of DNA molecules through microfabricated nanopores with applications to genomic analysis [26]; and many others.

While these phenomena are used ubiquitously in many micro and nanofluidic devices, their precise modeling is highly complex owing to the nontrivial coupling between electrical, chemical and mechanical effects, and is typically limited to relatively simple settings in which simplifying assumptions such as weak field, thin Debye layer, etc. apply. For more complex problems in which these assumptions break down, detailed or accurate models are often still lacking. This is especially true at the nanoscale, as non-continuum effects sometimes become significant, and as the characteristic thickness of the electrical double layers becomes of the same order as the geometric length scales of the device. Modeling becomes particularly difficult when either particles or macromolecules are present, as these can possess their own electrical double layer, and may interact both electrically and hydrodynamically with the device boundaries. Previous approaches to tackle these problems have included continuum models based on the Poisson-Nernst-Planck equations [20], and atomic simulations using molecular dynamics algorithms [17]. While both approaches have their merits, neither of them is easy to use or performs particularly well in applications requiring the modeling of electrokinetic transport in strong confinement and over long time scales.

In this work, we propose to develop a number of novel numerical and
computational tools to address some of these issues. Our models will center around a new approach based on a Langevin equation for diffuse charge dynamics in nanofluidic devices, which incorporates features from both continuum and atomistic methods. This approach, which we present in more detail in chap. 2, will be applied to model electro-osmotic flows in nanochannels. We anticipate that the computational tools developed will be widely applicable to model many different engineering processes involving diffuse charges in confined devices.

1.1 Background

The phenomenon of electro-osmosis has been known for a long time and is illustrated in Fig. 1.1 [27, 28, 20]. In a micro or nanochannel, channel walls typically possess a native charge, which attracts ions of opposite sign (counterions) in the neighboring electrolyte. These ions accumulate near the charged surface, resulting in the formation of a diffuse charge cloud, also known as a Debye layer or electrical double layer (EDL). When an electric field \( E_0 \) is applied, the net excess charge in the EDL is subject to an electric force which drives the motion of the fluid relative to the fixed surface. In

![Figure 1.1: Electro-osmotic flow.](image)
a channel, this phenomenon results in a so-called electro-osmotic (EO) flow. The characteristic thickness $\lambda_D$ of the Debye layer, which is determined by the balance between ion attraction by the charged surface and ion diffusion, is typically of the order of 10-100 $\mu$m in aqueous solutions. When this thickness is much less than the channel width (as is typical in the case of microchannels), the effect of the electrical force inside the EDL on the flow outside the EDL is well captured by an effective slip velocity $u_s$, given by the Helmholtz-Smoluchowski equation [29]: $u_s = (\epsilon \zeta / \mu)E_0$, where $\epsilon$ and $\mu$ are the permittivity and viscosity of the fluid, and $\zeta$ is the zeta-potential or potential drop across the EDL, and is considered a material constant. This slip velocity can then be shown to drive a potential flow outside of the EDL, which is a plug flow in a unidirectional microchannel [20].

The situation becomes significantly more complex when the Debye thickness $\lambda_D$ is of the same order as the characteristic geometric scale of the device, as is the case typically in nanochannels [30, 31, 32]. In this case, the Helmholtz-Smoluchowski equation is no longer valid and the exact ionic distribution in the channel must be determined in order to evaluate the corresponding force distribution acting on the fluid. The classical approach for obtaining this distribution is by solution of the Nernst-Planck equations, which model the ionic conservation (under the effects of diffusion, convection and electromigration), and of the Poisson’s equation for the determination of the electrical potential in the solution. Knowledge of the excess charge distribution then allows one to obtain the resulting flow velocity field from the Stokes equations including an electric body force. This approach was followed in a number of classical papers on EO flow in nanochannels [33, 34, 35, 36], as well as in a number of more recent studies, e.g. [37, 38, 39, 40].

While models based on Poisson-Nernst-Planck (PNP) equations manage to capture qualitative trends in nanochannels, they often fail at providing quantitative results that agree with experiments [30, 31, 32]. This is especially true in highly confined environments in which EDLs from opposite walls overlap. Several reasons can be invoked for the breakdown of these models. Specifically, the PNP equations are not able to capture discrete effects, which become more important at very small scales. For instance, steric effects due to the finite size of ions in electrolytes can become significant inside double layers as has been shown in previous studies [41, 42, 43], and are not typically accounted for in continuum models, which can often predict
ionic concentrations well beyond the close packing limit. While some corrections to these models have been proposed to remedy this problem [41, 42], the precise structure of the double layers can not be captured short of using discrete models for the ionic distributions.

One approach to capture the precise structure of the double layers is obviously molecular dynamics (MD) simulations [44], in which the exact motions of solvent molecules and salt ions are solved for using Newtons equations of motion. MD simulations have been applied successfully to simulate electrokinetic flow in nanochannels, e.g. [45, 46, 47, 48, 49]. A great advantage of this approach is that it provides detailed information on the structure of the double layers inside the channels down to molecular length scales, and naturally accounts for non-continuum effects such as steric effects, structuring of the fluid near the walls, etc. Such simulations, however, are extremely costly owing to the very large number of degrees of freedom (corresponding to the positions of all the atoms in the channel) and to the very short time scales that need to be resolved. As a result, only very thin and short channels with simple geometries have been simulated, over time scales that are typically much shorter than the relevant dynamic time scales in problems involving particles or macromolecules. In Chap. 2 we propose a new approach to model electrokinetic flows in highly confined environments based on a Langevin description of the excess charge dynamics, that incorporates features from both the PNP and MD models.

1.2 Overview

The theory and formulation of our model based on a Langevin equation will be presented in detail in Chap. 2. Chap. 3 outlines the numerical algorithms to solve the model, and also presents our development of an efficient algorithm for the confined Stokes equation with double periodicity. Chap. 4 shows the results and discussion of simulations of the model problem for double layer charging, with comparison between Langevin approach and continuum theory, and further illustrates more physics revealed by this approach, which the continuum theory cannot predict. Chap. 5 summarizes the conclusions and potential applications and future work.
CHAPTER 2
THEORY

This chapter briefly outlines the continuum dilute solution theory that is traditionally used to describe the electro-diffusion of ions and electrokinetic phenomena. The Langevin approach is detailed in Sec. 2.2. The formulations for multi species are also described for both the continuum and Langevin approaches. And finally, the theory for electro-osmosis is discussed for both approaches.

2.1 The Continuum Approach

2.1.1 The Poisson-Boltzmann equations

The standard model of electro-diffusion is based on the assumption that the ions of a species \( i \) in a dilute solution are in quasi-thermal equilibrium with a Boltzmann distribution:

\[
c_i = c_0^i e^{-\frac{z_i e \phi}{K T}},
\]

where \( c_0 \) is a reference concentration, taken to be the mean charge concentration, \( z_i \) is the valence, \( e \) is the elementary charge, and \( K T \) is the thermal energy of the liquid. The electrostatic potential \( \Phi \) is given (in a mean-field approximation) by Poisson’s equation:

\[
\varepsilon_0 \nabla^2 \Phi = - \sum_i z_i e c_i.
\]

Combining Eqn. (2.1) and Eqn. (2.2), we get the Poisson-Boltzmann equation:

\[
\varepsilon_0 \nabla^2 \Phi = - \sum_i z_i c_0^i e^{-\frac{z_i e \phi}{K T}}.
\]
Now we define an important parameter Debye screening length referred to in Chap. 1. For a symmetric binary \((z : z)\) electrolyte in a one-dimensional geometry, with \(c_0\) being the reference charge concentration, the Debye screening length is given by

\[
\lambda_D = \sqrt{\frac{\varepsilon_0 kT}{2z^2 e^2 c_0}}. \tag{2.4}
\]

It gives the characteristic width obtained by nondimensionalizing the PB equation, and is the measure of a charge carrier’s net electrostatic effect in solution.

### 2.1.2 The Poisson-Nernst-Planck equations

When the assumption of quasi-thermal equilibrium cannot be made, such as during transient processes, or in electrolytes subject to time-dependent applied voltages, the Boltzmann distribution no longer holds, and the description must now include a conservation equation for each ionic species.

Define ion flux velocity:

\[
v_i = -\frac{D_i}{kT} z_i e \nabla \Phi - D_i \nabla \ln c_i + u, \tag{2.5}
\]

where \(D_i\) is the diffusivity of species \(i\), and \(u\) is fluid velocity.

The classical description for charge dynamic comes from the Poisson-Nernst-Planck equations, which consist of Poisson’s equation Eqn. (2.2), and mass conservation laws for the ions:

\[
\frac{\partial c_i}{\partial t} + \nabla \cdot (c_i v_i) = 0. \tag{2.6}
\]

Since \(\nabla \cdot u = 0\), we can get the PNP equations:

\[
\varepsilon_0 \nabla^2 \Phi = -\sum_i z_i e c_i, \tag{2.7a}
\]

\[
\frac{\partial c_i}{\partial t} + \nabla \cdot \left(-\frac{D_i}{kT} z_i e \nabla \Phi - D_i c_i \nabla \ln c_i + u \cdot \nabla c_i \right) = 0. \tag{2.7b}
\]

Now we define the following dimensionless variables:

- \(c = \frac{c^+ + c^-}{2c_0}\) : ion concentration
- \(\rho = \frac{c^+ - c^-}{2c_0}\) : charge density
And introduce two important dimensionless parameters:

- \( \frac{\lambda_p}{L} \): ratio of Debye Length to domain size, which is usually very small
- \( V = \frac{z e V}{kT} \): dimensionless voltage given by the boundary condition

The solution of the PNP equations is uniquely determined by these two parameters.

In a 1-D geometry, the dimensionless PNP equations are written as

\[
\begin{align*}
\frac{\partial c}{\partial \tau} &= \frac{\lambda_D}{L} \sum_x \left( \frac{\partial c}{\partial x} + \rho \frac{\partial \phi}{\partial x} \right), \\
\frac{\partial \rho}{\partial \tau} &= \frac{\lambda_D}{L} \sum_x \left( \frac{\partial \rho}{\partial x} + c \frac{\partial \phi}{\partial x} \right), \\
- \left( \frac{\lambda_D}{L} \right)^2 \sum_x \frac{\partial^2 \phi}{\partial x^2} &= \rho.
\end{align*}
\] (2.8)

with boundary conditions:

\[
\phi(0) = 0, \quad \phi(1) = V. \tag{2.9}
\]

The classical continuum model of the PNP equations is often used to model the diffuse layer. But at large applied voltage, it is limited due to the exponential sensitivity of counterion concentration to voltage. For instance, there exists a maximum possible concentration of ions near a surface, forming a close packing, in which case the classical Poisson’s Boltzmann equation will over predict the concentration.

2.1.3 The Modified Poisson-Boltzmann equations

To overcome the limitation of PB equation, modified Poisson-Boltzmann equations have been proposed [41]. The basic formulation is as follows.

Let the maximum ion concentration be \( c_{\text{max}} \) due to the finite size of ion. We also introduce another parameter, \( \nu = \frac{c_0}{c_{\text{max}}} \), ratio of the mean to maximum
density. It is the mean volume fraction of ions in the bulk, and a natural measure of non-diluteness. This parameter $\nu$, along with dimensionless voltage $V$, controls the importance of steric effects.

The concentrations in the diffuse layer as a function of the electrostatic potential are given by the modified Boltzmann distribution:

$$c_\pm = \frac{c_0 e^{\mp \phi/KT}}{1 + 2\nu \sinh^2 \left( \frac{ze\phi}{2KT} \right)}.$$  \hfill (2.10)

And the potential satisfies the modified Poisson-Boltzmann “MPB” equation:

$$\nabla^2 \phi = \frac{zec_0}{\varepsilon} \frac{2 \sinh \frac{ze\phi}{2KT}}{1 + 2\nu \sinh^2 \left( \frac{ze\phi}{2KT} \right)}.$$  \hfill (2.11)

The MPB equation models steric effects based on modifications of the Poisson Boltzmann description of dilute solutions, and can predict some of the consequences of the finite size of the ions. However, being a continuum model, it still fails to model some discrete behavior, such as ion packing near the wall.

2.2 The Langevin Approach

As explained in Chap. 1, existing models for electro-osmotic flow in highly confined devices suffer from several limitations. Continuum models based on the PNP equations are highly complex and difficult to solve even numerically, and fail to capture a number of phenomena which result from the discrete nature of the electrical double layers. Atomistic models based on MD simulations provide excellent resolution but are extremely costly and only allow the simulation of very small devices with simple geometries over short time scales.

The basis for the proposed methodology is the observation that the solution of the Nernst-Planck equations is strictly equivalent to an ensemble average over a collection of charged Brownian particles (representing the ionic species in the EDL) undergoing a stochastic motion satisfying an appropriate Langevin stochastic differential equation.

Because Eqn. (2.6) is simply an advection-diffusion equation, its solution is equivalent to an ensemble average over trajectories of Brownian particles.
obeying the following Langevin equation, for instance for a charged ion of index \( i \) with position \( \mathbf{x}_i \):

\[
\mathbf{d}\mathbf{x}_i = (-\frac{D}{KT}z\mathbf{e}\nabla\phi(\mathbf{x}_i) + \mathbf{u})dt + \sqrt{2Ddt} \mathbf{n}, \quad i = 1, \ldots, N, \tag{2.12}
\]

where the \(-\frac{D}{KT}z\mathbf{e}\nabla\phi(\mathbf{x}_i)\) and \(\mathbf{u}\) represent electromigration and convection respectively, while the last term contains a standard random Gaussian variable \(\mathbf{n}\) with zero mean and unit variance. It plays the role of diffusion.

In this case, the electric potential now satisfies a discrete version of Poisson’s equation:

\[
\nabla^2 \phi = -\frac{ze}{\varepsilon_0} \sum_n \pm \delta(\mathbf{x} - \mathbf{x}_n^\pm), \tag{2.13}
\]

where the sum is now over all the ions in the solution and \(\delta\) denotes the Dirac delta function.

Using the dimensionless parameters \(\frac{\lambda_D}{L}\) and \(V\), we can get the dimensionless Poisson and Langevin equations:

\[
\left(\frac{\lambda_D}{L}\right) \nabla^2 \phi = -\frac{1}{2N} \sum_n q_n \delta(\mathbf{x} - \mathbf{x}_n), \tag{2.14a}
\]

\[
\mathbf{d}\mathbf{x}_i = \frac{\lambda_D}{L} \nabla\phi(\mathbf{x}_i)d\tau + \sqrt{\frac{2\lambda_D}{L}d\tau} \mathbf{n}, \quad i = 1, \ldots, N, \tag{2.14b}
\]

with boundary conditions:

\[
\phi(0) = 0, \quad \phi(1) = V. \tag{2.15}
\]

This formulation can be used to simulate double layer charging as follows. First, the charge distribution in the electrolytes is determined by Brownian dynamics simulations based on the Langevin formulation of the Nernst-Planck equations. Electric interactions between ions are modeled either from a mean-field description of the induced field obtained by extrapolating the excess charges to a grid, or directly as Coulomb interactions between point charges (together with an efficient particle-mesh algorithm called SPME discussed below in Sec. 3.2). The Langevin equation is then used to advance the charges.

The advantages of this approach with respect to the methods discussed in Chap. 1 are twofold:
The discrete nature of the ions, which may become important especially in highly confined environments such as nanocapillary array membranes or nanopores is captured naturally. In particular, non-continuum effects such as steric interactions could easily be included by addition of a short-range repulsive potential.

The ion dynamics are captured on the diffusive time scale, which is much longer than the ballistic time scale that molecular dynamics simulations need to resolve. This should allow probing the dynamics over much longer times than achieved by MD and may prove to be particularly useful for the study of unsteady problems.

The Langevin approach will first be benchmarked against well defined test cases, such as electro-osmosis in straight nanochannels, for which analytical solutions of the PNP equations exist. Ultimately, it will be improved to include more complex phenomena including discrete effects that are not easily captured by continuum models, such as ion adsorption at surfaces, steric interactions between ions, etc.

2.3 Multi Diffusivity and Multi Valence

When there are multiple species in solution, each with its own diffusivity and valence, we need to slightly modify our model.

Let $z_0$ and $D_0$ be the reference valence and diffusivity, $c_0$ being the reference concentration, we also has the reference Debye Layer length:

$$\lambda_{D_0} = \sqrt{\frac{\varepsilon_0 kT}{2z_0^2 e^2 c_0}}.$$  \hspace{1cm} (2.16)

For dimensionless time, length and potential, $\tau$, $x$, and $\phi$, we have

- $\tau = \frac{D_0}{\lambda_{D_0} L} t :$ time
- $x = L X :$ length
- $\phi = \frac{z_0 e}{kT} \Phi :$ potential
For the concentration of the various species, $c_i'$ denotes the dimensional concentration, the dimensionless concentration $c_i$ can be defined by

$$c_i = \frac{c_i'}{2c_0}. \quad (2.17)$$

Also define dimensionless parameters:

- $\frac{D_i}{D_0}$: ratio of diffusivity
- $\frac{z_i}{z_0}$: ratio of valences

Based on these dimensionless variables, we can derive the PNP and Langevin equations for multi species. The full derivation can be found in Appendix D, the brief outlines and results are listed in the following.

### 2.3.1 PNP of Multi Species

We can define the dimensionless charge density:

$$\rho = \frac{1}{2z_0c_0} \sum_i z_i c_i' = \sum_i \frac{z_i}{z_0} c_i. \quad (2.18)$$

Now we have the Poisson’s equation, and PNP for each species:

$$-\left(\frac{\lambda D_0}{L}\right)^2 \nabla^2 \phi = \rho = \sum_i \frac{z_i}{z_0} c_i, \quad (2.19a)$$

$$\frac{\partial c_i}{\partial \tau} = \frac{D_i}{D_0} \frac{\lambda D_0}{L} \frac{\partial}{\partial x} \left( \frac{\partial c_i}{\partial x} \pm \frac{z_i}{z_0} c_i \frac{\partial \phi}{\partial x} \right). \quad (2.19b)$$

### 2.3.2 Langevin Equation of Multi Species

The Poisson’s equation for the Langevin approach is unchanged, while the Langevin equation is modified:

$$\left(\frac{\lambda_d}{L}\right) \nabla^2 \phi = -\frac{1}{2N} \sum_n q_n \delta(x - x_n), \quad (2.20a)$$

$$d\mathbf{x}_i = \pm \frac{D_i}{D_0} \frac{z_i}{z_0} \frac{\lambda D_0}{L} \nabla \phi d\tau + \sqrt{2 \frac{D_i}{D_0} \frac{\lambda D_0}{L} d\tau} \mathbf{n}, \quad i = 1, \ldots, N. \quad (2.20b)$$
From the above equations for multi species dynamics Eqn. (2.19) and Eqn. (2.20), we can see the different diffusivities and valences can affect the speed of the charging. Higher diffusivity and higher valence will result in faster charging process. And from Eqn. (2.19b), we can conclude that the steady state charge density does not depend on diffusivity, but will be affected by the valence. All these will be confirmed by our simulation results in Sec. 4.4.1 and Sec. 4.4.2.

2.4 Electro-Osmotic Flow

The phenomenon of electro-osmosis introduced in Chap. 1 can be modeled by either the continuum or Langevin approach, as we discuss below.

2.4.1 Stokes Equation For Continuum Model

Given the number density distribution in the channel, the flow in the continuum model is governed by Stokes equation:

\[-\nabla^2 \mathbf{u} + \nabla p + \rho \nabla \phi = 0,\]
\[\nabla \cdot \mathbf{u} = 0,\]

where the \(\rho \nabla \phi\) term acts as a body force, and includes both the external field \(\mathbf{E}\) and electrical interactions between ions.

In the \(x\) direction, \(-\nabla \phi\) is the external field \(\mathbf{E}_x\). And the flow velocity is only along \(x\) direction, its depends solely on \(z\). When there is no pressure gradient, we have the one-dimensional Stokes equation and Poisson's equation:

\[-\frac{\partial^2 u_x}{\partial z^2} + E_x \rho = 0,\]
\[\nabla^2 \phi + \rho = 0.\]

We conclude that the fluid velocity profile adopts the same shape as the electrical potential. We will show in Sec. 4.5 a comparison of the flow velocity with the electrical potential.
2.4.2 Stokes Equation For Langevin Approach

In the Langevin approach, with an external electric field $E_x$ applied, each ion exerts a point force on the fluid, which will drive a fluid flow. This fluid flow may be obtained by solution of the Stokes equations including discrete forcing terms corresponding to these forces:

$$-\nabla^2 u + \nabla P + \sum_n F_n \delta(r - r_n) = 0, \tag{2.23a}$$

$$\nabla \cdot u = 0, \tag{2.23b}$$

where the point force $F_n$ includes external field $E$ and electrical interactions between ions.

The calculation of electric and hydrodynamic interactions between the excess ions is the most expensive step of the simulation method and would render the simulations untractable if performed directly. To accelerate the simulations, a Smooth Particle Mesh Ewald (SPME) algorithm will be used, the detailed description of which will be discussed in Sec. 3.3.1. The resultant calculated flow will be shown in Sec. 4.5.
CHAPTER 3

METHODS

This section discusses the method we use to solve the dimensionless Poisson’s equation with boundary conditions:

\[ \nabla^2 \phi = \sum_n q_n \delta(x - x_n), \quad (3.1a) \]

\[ \phi|_{z=0} = 0, \quad \phi|_{z=L} = V, \quad (3.1b) \]

as well as the algorithm we use to solve Stokes flow with point forces:

\[ -\nabla^2 u + \nabla P + \sum_n F_n \delta(r - r_n) = 0, \quad (3.2a) \]

\[ \nabla \cdot u = 0, \quad (3.2b) \]

with no-slip boundary conditions at the walls:

\[ u|_{z=0} = u|_{z=L} = 0. \quad (3.3) \]

For both problems, we impose 2D periodicity in the \( x \) and \( y \) directions.

3.1 Using FFT to Solve Poisson’s Equation

An intuitive way to calculate the electrical interactions between ions is using FFT to solve Poisson’s equation. The solution may be sought as the superposition of two potentials \( \phi_h \) and \( \phi \). \( \phi_h \) satisfies Laplace’s equation with no point charges in the domain, and the given boundary condition on the walls in the \( z \) direction (imposed potential). And \( \phi \) satisfies Poisson’s equation with all the point charges inside the domain, with homogeneous boundary conditions on the walls in the \( z \) direction. \( \phi_h \) is easily solved analytically, while \( \phi \) is solved for using FFT as follows:
1. distribute charges onto a Cartesian grid by linear interpolation,

2. use FFT to solve Poisson’s equation for the potential,

3. take the gradient of the potential by finite difference to obtain the electrical field at the grid points,

4. back interpolate to get the electrical field at the positions of the ions.

Fig. 3.1 illustrates the assignment of charge by linear interpolation.

3.1.1 Solving Poisson’s equation

We wish to solve Poisson’s equation with homogeneous boundary conditions:

\[- \left( \frac{\lambda L}{L} \right)^2 \nabla^2 \phi = \rho, \quad (3.4a)\]

\[\phi \big|_{z=0,L} = 0. \quad (3.4b)\]

Since the potential \( \phi \) and charge density \( \rho \) are periodic along \( x \) and \( y \), we can write \( \phi \) and \( \rho \) as superpositions of Fourier modes along these directions. Further, since the potential and charge density vanish at the bottom and top walls, we can write \( \phi \) and \( \rho \) as superpositions of sines of various wavelengths along \( z \). That is:

\[
\rho(x, y, z) = \sum_{k=1}^{\infty} \sum_{i=-\infty}^{\infty} \sum_{j=-\infty}^{\infty} R_{ijk} e^{2\pi i(i+x+j+y)} \sin(\pi k z), \quad (3.5a)
\]
ϕ(x, y, z) = \sum_{k=1}^{\infty} \sum_{i=-\infty}^{\infty} \sum_{j=-\infty}^{\infty} \Phi_{ijk} e^{2\pi i(x+iy)} \sin(\pi k z). \quad (3.5b)

Invoking orthogonality of Fourier modes, we can solve for the coefficients:

\Phi_{ijk} = \frac{R_{ijk}}{\pi^2 (4i^2 + 4j^2 + k^2)} \left( \frac{L}{\lambda_d} \right)^2. \quad (3.6)

With ρ known from the charge assignment, we can solve for Φ.

3.1.2 Comments on FFT method

In spite of the simplicity of this approach, it suffers from the low accuracy for the electrical forces. Near-field interactions cannot be captured. So we use another approach to calculate the electrical interactions, called SPME (Smooth Particle Mesh Ewald) algorithm.

3.2 SPME (Smooth Particle Mesh Ewald) Approach

SPME is a well established method in molecular dynamics simulations [50, 51, 52], and was recently extended to calculate hydrodynamic interactions between particles in Stokes flow [53]. Its cost is in \( O(N \log N) \) with the number \( N \) of particles, and it has been shown to result in a very significant increase in efficiency with respect to direct methods [53]. It is an accurate and efficient way to calculate interactions in an \( x, y, z \) periodic domain. Here we first introduce the SPME for electrical interactions, and later in Sec. 3.3.1 we see how this method can be generalized to Stokes interactions.

In this approach, the potential is treated as the superposition of three parts:

\[ \Phi = \phi_h + \phi + \phi_b, \quad (3.7) \]

where

1. \( \phi_h \) satisfies Laplace’s equation with periodic boundary conditions along \( x \) and \( y \), and the given boundary condition on the walls in the \( z \) direction (imposed potential),
2. \( \phi \) satisfies Poisson’s equation Eqn. (3.1a) with 3D periodic boundary conditions, this is obtained by SPME.

3. \( \phi_b \) satisfies Laplace’s equation with periodic boundary conditions along \( x \) and \( y \), and \( \phi_b|_{z=0} = \phi_b|_{z=L} = -\phi|_{z=0} = -\phi|_{z=L} \).

The sum of the three potentials \( \Phi \) then satisfies Eqn. (3.1a) and the boundary conditions. \( \phi_b \) can be solved for analytically; \( \phi \) is solved for using SPME algorithm as below, and \( \phi_b \) is solved using the FFT method.

### 3.2.1 Ewald Sum

The Ewald Sum is a way to calculate interactions in an \( x, y, z \) periodic domain. Based on Ewald sum, SPME can be developed in subsequent sections.

The method begins with splitting a \( \delta \)-function (representing a point charge here) into two parts, one is the \( \delta \)-function minus a Gaussian distribution (with mean in \( x_n \)): \( \delta(x_n) - N(x_n) \), where \( \delta(x_n) \) and \( N(x_n) \) integrate to the same value, and the other being the Gaussian distribution \( N(x_n) \). See Fig. 3.2 for illustration.

![Figure 3.2: Splitting of \( \delta \)-function.](image)

The electrical potential is by this way split into two parts, which converge fast in real space (short range interaction) and Fourier space (long range interaction) respectively:

\[
\phi = \phi^S + \phi^L. \tag{3.8}
\]

The short range interaction \( \phi^S \) and long range interaction \( \phi^L \) are given by

\[
\phi^S(x) = \frac{1}{4\pi \varepsilon_0} \sum_p \sum_{j=1}^{N} \frac{q_j}{|x - x_j + p|} \text{erfc} \left( \frac{|x - x_j + nL|}{\sqrt{2}\alpha} \right), \tag{3.9a}
\]
\[ \phi^L = \frac{1}{\tau_0 \varepsilon_0} \sum_k \sum_j^N e^{-\alpha^2 k^2/2} q_j e^{2\pi i k \cdot x_j}. \] (3.9b)

where \( p = nL \), represents the images of each ion, and \( \tau_0 \) is the volume of the cell. The Ewald coefficient \( \alpha \) in Eqn. (3.9a) is a user-defined parameter that determines the relative importance of the two sums: its choice is typically dictated by cost considerations. To calculate the electrical field at the position of particle \( i \), we need to take the derivative of the electrical potential:

\[ E_i = \frac{\partial \phi}{\partial x_i} = -\frac{\partial \phi^S}{\partial x_i} - \frac{\partial \phi^L}{\partial x_i}. \] (3.10)

Define the structure factor, \( \hat{q}(k) \) as the Fourier transform of the distribution of point charges:

\[ \hat{q}(k) = \sum_j^N q_j e^{2\pi i k \cdot x_j}. \] (3.11)

After some algebra, and nondimensionalization, we have

\[ -\nabla \phi(x_m) = \sum_p \sum_{n=1}^N A(\alpha, x_m - x_n + p) q_n + \sum_{k \neq 0} e^{-2\pi i k \cdot x_m} B(\alpha, k) \hat{q}(k). \] (3.12)

The two vectors \( A \) and \( B \) are given by

\[ A(\alpha, x) = \frac{1}{2\alpha^2} \psi_{\frac{1}{2}} \left( \frac{\pi r^2}{\alpha} \right) x, \] (3.13)

\[ B(\alpha, k) = \frac{\alpha}{2\tau_0} \psi_0(\pi \alpha k^2) k. \] (3.14)

where, \( r^2 = ||x||^2 \) and the functions \( \psi_\nu \) are special functions given by

\[ \psi_{\frac{1}{2}}(x) = \frac{e^{-x}}{x} + \sqrt{\frac{\pi}{2x^2}} \text{erfc}\sqrt{x}, \quad \psi_0(x) = \frac{e^{-x}}{x}. \] (3.15)

### 3.2.2 SPME for Electrical Field

The short range part is calculated in real space. The exponential decay of the vector \( A \) can be exploited to restrict the evaluation of the sum to close particle pairs. Given a tolerance \( \epsilon \) and a cutoff radius \( r_c \), the Ewald coefficient
\( \alpha \) can be chosen to make all the coefficients of \( A(\alpha, x) \) less than \( \epsilon \) whenever \( \|x\| > r_c \). Once \( \alpha \) is obtained following this procedure, the real sum in Eqn. (3.9a) only needs to be performed over the particles located within a sphere of radius \( r_c \), i.e., over a small number independent of the system size. The evaluation of the sum at all the particles locations \( x_i \) then has an \( O(N) \) cost, with a constant of proportionality that can be adjusted through the cutoff radius. This near field interaction is done by the method of “Cell List”, which divides the whole domain into smaller cubic cells, and assigns ions to each cell. When searching for the nearby ions, only the neighboring cells are searched. In this way the near field calculation is efficiently achieved.

The real gain is achieved in the evaluation of the Fourier sum. The presence of the structure factors \( \hat{q}(k) \) suggests use of the fast Fourier transform algorithm. As the particles can be located anywhere inside the unit cell, prior interpolation to a Cartesian grid is necessary. This can be done formally using Cardinal B-splines. Charges are distributed onto grids using B-spline. And FFT is used to approximate the structure factor \( \hat{q}(k) \), and Cardinal B-splines interpolation is used again to calculate electrical forces at each particle position. The details of the algorithm can be found in [50].

### 3.2.3 Enforcement of Electrical Boundary Condition: the “Boundary Correction” Method

To satisfy the zero boundary condition on the wall, we solve an auxiliary problem, which negates the value of the potential on the wall:

\[
\nabla^2 \phi_b = 0, \quad (3.16a)
\]

\[
\phi_b|_{z=0} = \phi_b|_{z=L} = -\phi|_{z=0} = -\phi_0. \quad (3.16b)
\]

Since \( \phi_0 \) and \( \phi_b \) are periodic along \( x \) and \( y \), we can expand them as Fourier series:

\[
\phi_0(x) = \sum_k \phi_{0,k}(z)e^{-2\pi ik \cdot R}, \quad (3.17a)
\]

\[
\phi_b(x) = \sum_k \phi_{b,k}(z)e^{-2\pi ik \cdot R}. \quad (3.17b)
\]

where \( k = (k_x, k_y) \) and \( R = (x, y) \).
Substituting this form into Laplace’s equation and invoking the orthogonality of modes corresponding to distinct wavenumbers, yields an ordinary differential equation:

\[
\frac{d^2 \phi_{b,k}}{dz^2} = 4\pi^2 k^2 \phi_{b,k}(z),
\]

where \( k^2 = k_x^2 + k_y^2 \). This ODE has the solution:

\[
\phi_{b,k} = A_k e^{2\pi k z} + B_k e^{-2\pi k z}.
\]

Now we apply the boundary conditions:

\[
\phi_b(z = 0) = \sum_k \phi_{0,k} e^{-2\pi ik \cdot R},
\]

yielding equations for \( A_k \) and \( B_k \):

\[
A_k + B_k = \phi_{0,k},
\]

\[
A_k e^{2\pi k L} + B_k e^{-2\pi k L} = \phi_{0,k},
\]

so that

\[
A_k = \frac{(1 - e^{-2\pi k L}) \phi_{0,k}}{e^{2\pi k L} - e^{-2\pi k L}}, \quad B_k = \frac{(e^{2\pi k L} - 1) \phi_{0,k}}{e^{2\pi k L} - e^{-2\pi k L}}.
\]

After substitution into (3.19), we get

\[
\phi_{b,k} = \sum_k \phi_{0,k} \frac{e^{2\pi k z} (1 - e^{-2\pi k L}) e^{-2\pi k z} + (e^{2\pi k L} - 1)e^{-2\pi ik \cdot R}}{e^{2\pi k L} - e^{-2\pi k L}}.
\]

Using these Fourier coefficients and applying FFT again, we can obtain \( \phi_b \) and satisfy the imposed wall potential.

### 3.3 Stokes Interactions

To simulate electro-osmotic, we need to compute the flow field in the doubly-periodic domain introduced in Sec. 2.4.2 with no-slip boundary condition. We superimpose two distinct Stokes problems adopting similar "Bound-
ary Correction” idea in the above section:

\[ \mathbf{u} = \mathbf{u}_{\text{SPME}} + \mathbf{u}_{\text{BC}}, \quad P = P_{\text{SPME}} + P_{\text{BC}}. \]  

(3.24)

The velocity and pressure fields \((\mathbf{u}_{\text{SPME}}, P_{\text{SPME}})\) solve the inhomogeneous Stokes equations (3.2) forced by the singular point forces \(\mathbf{F}_n\), but subject to periodic boundary conditions in all three dimensions. This first problem can be solved efficiently and with high accuracy using the SPME algorithm, as summarized in Sec. 3.3.1.

Quite obviously, this periodic solution does not satisfy the desired no-slip condition at \(z = 0, L\), but rather exhibits a nonzero velocity field at these locations, which we denote by \(-u_1(x, y)\) and \(-u_2(x, y)\). This nonzero velocity at the walls is canceled by the second problem by “Boundary Correction” method, which solves the homogeneous Stokes equations subject to 2D periodic boundary condition along the \(x\) and \(y\) directions and to the inhomogeneous Dirichlet boundary condition:

\[ \mathbf{u}_{\text{BC}}(x, y, z)|_{z=0} = u_1(x, y), \]  

(3.25a)

\[ \mathbf{u}_{\text{BC}}(x, y, z)|_{z=L} = u_2(x, y). \]  

(3.25b)

As we explain in Sec. 3.3.2, this problem can be solved analytically after two-dimensional Fourier transformation of the flow variables and boundary velocity data.

\[ \begin{align*}
-\nabla^2 \mathbf{u} + \nabla P &= \sum_n \mathbf{F}_n \delta(r - r_n) \\
\nabla \cdot \mathbf{u} &= 0
\end{align*} \]

Figure 3.3: Point-forces-induced boundary flow.
Figure 3.4: Flow with specified boundary conditions.

See Fig. 3.3 and Fig. 3.4 for an illustration of this method. First, a point-forces-induced flow is computed by SPME, giving a nonzero flow on the boundary, see Fig. 3.3. Then a flow with specified boundary conditions to negate the boundary flow is solved and superimposed to obtain the solution of the full equation, see Fig. 3.4 for the flow with specified boundary conditions.

3.3.1 SPME for the Stokes Equations

SPME can be generalized for Stokes interactions to calculate the flow in an $x, y, z$ periodic domain induced by point forces. Details can be found in Appendix A and [53].

For point-forces-induced flow, the velocity is given by

$$u_{\text{SPME}}(x_m) = \sum_p \sum_{n=1}^{N} A_F(\alpha, x_m - x_n + p)F_n + \sum_{k \neq 0} e^{-2\pi i k \cdot x_m} B_F(\alpha, k)\hat{F}(k). \quad (3.26)$$

The two tensors $A_F$ and $B_F$ are given by

$$A_F(\alpha, x) = \frac{\pi}{\alpha^2} \psi_1 \left( \frac{\pi r^2}{\alpha} \right) (r^2 I + x \otimes x) - \frac{2}{\alpha^2} e^{-\frac{\pi r^2}{\alpha}} I, \quad (3.27)$$

$$B_F(\alpha, k) = \frac{\pi \alpha^2}{\tau_0} \psi_1 (\pi \alpha k^2)(k^2 I - k \otimes k), \quad (3.28)$$
where \( r^2 = \|x\|^2 \), and the functions \( \psi_\nu \) are special functions given by

\[
\psi_2(x) = \frac{e^{-x}}{x} + \frac{\sqrt{\pi}}{2x^2} \text{erfc}\sqrt{x}, \quad \psi_1(x) = \frac{e^{-x}}{x^2}(1 + x). \tag{3.29}
\]

Observe that the two tensors \( A_F \) and \( B_F \) decay exponentially with respect to \( r^2 \) and \( k^2 \), respectively, which ensures rapid convergence of the sums.

Fig. 3.5 shows the streamline of one point force in the \( x \) direction, located at the center of the domain. It should be noted that on the boundary the velocity is not zero, and the algorithm introduced in the next section will be applied to enforce the no-slip boundary condition.

![Figure 3.5: Flow due to a point force in a 3D periodic domain](image)

3.3.2 Enforcement of No-Slip Boundary Condition: the “Boundary Correction” Method

The auxiliary solution \((u_{BC}, P_{BC})\) serves to correct the 3D periodic solution so as to satisfy the no-slip condition at \( z = 0, L \). It solves the homogeneous Stokes equations:

\[
-\nabla^2 u_{BC} + \nabla P_{BC} = 0, \tag{3.30a}
\]

\[
\nabla \cdot u_{BC} = 0, \tag{3.30b}
\]
subject to boundary conditions:

\[ u_{BC} = u_1 |_{(x,y,z=0)}, \]  
\[ u_{BC} = u_2 |_{(x,y,z=L)}. \]  

(3.31a)

(3.31b)

Expand the field and pressure in Fourier series:

\[ u_{BC} = \sum_{k_x} \sum_{k_y} \hat{u}_{BC}(k_x, k_y, z) e^{2\pi i (k_x x + k_y y)}, \]  
\[ P_{BC} = \sum_{k_x} \sum_{k_y} \hat{p}(k_x, k_y, z) e^{2\pi i (k_x x + k_y y)}, \]  
\[ u_1 = \sum_{k_x} \sum_{k_y} \hat{u}_1(k_x, k_y) e^{2\pi i (k_x x + k_y y)}, \]  
\[ u_2 = \sum_{k_x} \sum_{k_y} \hat{u}_2(k_x, k_y) e^{2\pi i (k_x x + k_y y)}. \]  

(3.32a)

(3.32b)

(3.32c)

(3.32d)

We then solve for \( \hat{u}_{BC}, \hat{v}_{BC} \) and \( \hat{w}_{BC} \) as:

\[ \hat{u}_{BC} = \frac{\cosh \left( q z - \frac{qL}{2} \right)}{\cosh \left( \frac{qL}{2} \right)} \left( \frac{\hat{u}_1 + \hat{u}_2}{2} \right) + \frac{\sinh \left[ q \left( z - \frac{L}{2} \right) \right]}{\sinh \left( \frac{qL}{2} \right)} \left( \frac{\hat{u}_2 - \hat{u}_1}{2} \right) \]  
\[ + \pi \frac{k_x}{q} (A \cdot C + B \cdot D), \]  
\[ \hat{v}_{BC} = \frac{\cosh \left( q z - \frac{qL}{2} \right)}{\cosh \left( \frac{qL}{2} \right)} \left( \frac{\hat{v}_1 + \hat{v}_2}{2} \right) + \frac{\sinh \left[ q \left( z - \frac{L}{2} \right) \right]}{\sinh \left( \frac{qL}{2} \right)} \left( \frac{\hat{v}_2 - \hat{v}_1}{2} \right) \]  
\[ + \pi \frac{k_y}{q} (A \cdot C + B \cdot D), \]  
\[ \hat{w}_{BC} = \frac{\cosh \left( q z - \frac{qL}{2} \right)}{\cosh \left( \frac{qL}{2} \right)} \left( \frac{\hat{w}_1 + \hat{w}_2}{2} \right) + \frac{\sinh \left[ q \left( z - \frac{L}{2} \right) \right]}{\sinh \left( \frac{qL}{2} \right)} \left( \frac{\hat{w}_2 - \hat{w}_1}{2} \right) \]  
\[ + \frac{1}{2} (A \cdot E + B \cdot F), \]  

(3.33a)

(3.33b)

(3.33c)

where \( C, D, E, F \) are functions of \( q \) and \( z \):

\[ C = \left( z - \frac{L}{2} \right) \sinh \left( q z - \frac{qL}{2} \right) - \frac{L}{2} \cosh \left( q z - \frac{qL}{2} \right) \tanh \left( \frac{qL}{2} \right), \]  
\[ D = \left( z - \frac{L}{2} \right) \cosh \left( q z - \frac{qL}{2} \right) - \frac{L}{2} \sinh \left( q z - \frac{qL}{2} \right) \coth \left( \frac{qL}{2} \right), \]  

(3.34a)

(3.34b)
\[
E = \left( z - \frac{L}{2} \right) \cosh \left( qz - \frac{qL}{2} \right) - \frac{L}{2} \sinh \left( qz - \frac{qL}{2} \right) \coth \left( \frac{qL}{2} \right), \quad (3.34c)
\]
\[
F = \left( z - \frac{L}{2} \right) \sinh \left( qz - \frac{qL}{2} \right) - \frac{L}{2} \cosh \left( qz - \frac{qL}{2} \right) \tanh \left( \frac{qL}{2} \right), \quad (3.34d)
\]
while \( A \) and \( B \) are functions of wavenumber \( k \) and boundary conditions \( u_1 \) and \( u_2 \):

\[
A = 2 \frac{2\pi i \left[ k_x (\hat{u}_1 + \hat{u}_2) + k_y (\hat{v}_1 + \hat{v}_2) \right] \sinh \left( \frac{qL}{2} \right) + q(\hat{w}_2 - \hat{w}_1) \cosh \left( \frac{qL}{2} \right)}{qL - \sinh(qL)}, \quad (3.35a)
\]
\[
B = -2 \frac{2\pi i \left[ k_x (\hat{u}_2 - \hat{u}_1) + k_y (\hat{v}_2 - \hat{v}_1) \right] \sinh \left( \frac{qL}{2} \right) + q(\hat{w}_1 + \hat{w}_2) \sinh \left( \frac{qL}{2} \right)}{qL + \sinh(qL)}, \quad (3.35b)
\]
The detailed derivation is listed in Appendix B.

Using these Fourier coefficients and applying FFT again, we can obtain the auxiliary flow to enforce the no-slip boundary condition.

### 3.4 Improved Convergence of the “Boundary Correction” Method with Image System

When a point force is very close to one of the walls, the force induces a large flow gradient on the boundary, and a very large number of Fourier modes will be needed to ensure the convergence. To improve the convergence of the “Boundary Correction” method, we add an image system to cancel most of the flow on the wall and reduce the flow gradient on the boundary, making it smoother. In this way, fewer Fourier modes for the “Boundary Correction” method will be needed, and the convergence can be improved.

#### 3.4.1 Image System for an Infinite Plane

For a point force above an infinite plane, the no-slip boundary condition can be enforced by adding an image system consisting of a point force in the opposite direction with the point force, a force dipole and a mass dipole [54]. See Fig. 3.6 for an illustration of the image system for an infinite plane.

In the image system, the magnitude of the point force is the same as the original point force \( F \), the force dipole is \( 2hF \), the mass dipole is \( 2h^2F \), where
Figure 3.6: Image system for an infinite plane.

$h$ is the distance from the plane. When the point force is along the plane or normal to the plane, the directions of force dipole and mass dipole are different, as shown in Fig. 3.6.

3.4.2 Image System in SPME

In periodic 3D boundary condition, the flow induced by force dipole and mass dipole can also be computed by generalizing SPME. The formulation also consists of two parts, a real sum and a Fourier sum, the derivation is detailed in Appendix A.

**Force Dipole**

The flow velocity induced by a force dipole is

\[
    u(x_m) = \sum_p \sum_{n=1}^N A_{Fd}(\alpha, x_m - x_n + p) Fd_n
    + \sum_{k \neq 0} e^{-2\pi i k \cdot x_m} B_{Fd}(\alpha, k) \hat{F}d(k). \tag{3.36}
\]
The two third order tensors $A_{Fd}$ and $B_{Fd}$ are given in index notation by

$$A_{Fdijk}(\alpha, x) = \frac{\pi}{\alpha^2} \psi_1 \left( \frac{\pi r^2}{\alpha} \right) \left( -x_k \delta_{ij} - \frac{3x_i x_j x_k}{r^2} + x_j \delta_{ik} + x_i \delta_{jk} \right)$$
$$- \frac{2\pi}{\alpha^2} e^{-\frac{x^2}{r^2}} \left( \frac{x_i x_j x_k}{r^2} - x_k \delta_{ij} \right), \quad (3.37)$$

$$B_{Fdijk}(\alpha, k) = -\frac{2\pi^2 i \alpha^2}{\tau_0} \psi_1(\pi \alpha k^2)(k^2 k_i \delta_{ij} - k_i k_j k_k), \quad (3.38)$$

where the functions $\psi_\nu$ are special functions given by

$$\psi_1(x) = \frac{e^{-x}}{x} + \frac{\sqrt{\pi}}{2 x^2 \tau^2} \text{erfc}(\sqrt{x}), \quad \psi_1(x) = \frac{e^{-x}}{x^2} (1 + x). \quad (3.39)$$

**Mass Dipole**

The flow velocity induced by a mass dipole is

$$u(x_m) = \sum_p \sum_{n=1}^N A_{Md}(\alpha, x_m - x_n + p) Md_n$$
$$+ \sum_{k \neq 0} e^{-2\pi i k \cdot x_m} B_{Md}(\alpha, k) Md(k). \quad (3.40)$$

The two second order tensors $A_{Md}$ and $B_{Md}$ are given by

$$A_{Md} = \frac{\pi}{3 \alpha^2} \psi_1 \left( \frac{\pi r^2}{\alpha} \right) \left( r^2 I - 3x \otimes x \right) - \frac{1}{3 \alpha^2} e^{-\frac{r^2}{\alpha}} I, \quad (3.41)$$

$$B_{Md} = \frac{\alpha \pi}{\tau_0} x \psi_1(\pi k^2 \alpha) k \otimes k, \quad (3.42)$$

where the functions $\psi_\nu$ are special functions given by

$$\psi_2(x) = \frac{e^{-x}}{x} + \frac{3 e^{-x}}{2 x^2} + \frac{3 \sqrt{\pi}}{4 x^2} \text{erfc}(\sqrt{x}), \quad \psi_0(x) = \frac{e^{-x}}{x}. \quad (3.43)$$

Fig. 3.7 shows the streamlines by force dipole and mass dipole located at the center of the domain.
Figure 3.7: Flows of mass dipole and force dipole.
3.4.3 Improvement of the “Boundary Correction” method with Image System

In order to include the image system, we add a padding of length $\sigma$ to each side of the simulation box in the $z$ direction. Usually the padding length is chosen to be the same cutoff $\alpha$ used in SPME, we place images of point forces near the wall in the padding area. A cutoff distance of $\delta$ is used for the inclusion of images. That means, if a point force is within a distance $\delta$ from the wall, the image system of this point force will be added in the padding area. See Fig. 3.8 for an illustration of the new simulation domain with the image system.

![Simulation domain with image system.](image)

Figure 3.8: Simulation domain with image system.

It should be pointed out that without the padding, the flow at $z = 0$ and $z = L$ are the same due to the periodicity in the $z$ direction, hence the expressions for the “Boundary Correction” Eqn. (3.33) can be simplified. However, when we include of the padding, the $z = 0$ and $z = L$ walls actually lie within the simulation domain, making the flow at the walls different. So we keep the expressions for the more general case when the two walls have different flow in Eqn. (3.33). The simplified expressions are given in Appendix B.

The improved performance of the “Boundary Correction” method will be discussed in Sec. 4.1.1.
3.5 Steric Interactions

3.5.1 Main Contact Algorithm

To model steric interactions between ions, we treat ions as hard spheres with their own radii. An event-driven idea is adopted to resolve the collisions between them. In this model, all particles are assumed to travel in straight lines with constant velocity over a given time step until a collision happens at time $t_p$. As ions $i$ and $j$ collide at time $t_p$, their relative radial velocities with respect to each other are eliminated, and their moving directions are also changed accordingly. Then we advance all the particles to the next collision time $t_{p+1}$, and resolve the collision between $m$ and $n$ at time $t_{p+1}$. Then we continue this loop, until all the collisions are resolved, or time step is reached.

The main challenge in this model is the determination of the ordered sequence of ion collisions. A data structure “Priority Queue”, also called “Heap”, is used to resolve this challenge. At any given time, the “Priority Queue” contains all future collisions that would happen, if each ion moves in a straight line with its current velocity. All these collisions events are sorted in the order of collision times. A main benefit of this data structure is that when a new collision is detected and added into the “Priority Queue”, the order of all the collisions (existing ones and the new one) can be maintained in an efficient way ($O(\log N)$). The insertion of collisions happens when ions collide with each other and change travel trajectory, and they may have new collisions which are not predicted. These new collisions are inserted into the “Priority Queue” right away, to ensure all the possible collisions are resolved. A flow chart of this algorithm is shown in Fig. 3.9.

3.5.2 Some Technical Issues

There are some technical issues to be considered in this algorithm:

“invalidated” collisions.

As ions collide and change velocities, the subsequent events associated with these colliding ions will no longer happen, since these ions have changed their trajectories. So we put marks on these “invalidated” collisions, and ignore them when they are encountered.
Figure 3.9: Hard sphere contact algorithm.
“impending” collision for one specific ion.

Each ion may have several possible collisions in the future. Say ion \( i \) will have two possible collisions with ion \( j \) at time \( t_j \) and ion \( k \) at time \( t_k \), and \( t_j < t_k \).

The simplest idea is to just keep the first collision in time (with ion \( j \) at \( t_j \)) and discard the rest (with ion \( k \) at \( t_k \)). But what if before time \( t_j \), ion \( j \) has already collided with another ion? In this case, the collision between ion \( i \) and \( j \) is an “invalidated” collision, which will not happen. And we need to redo the detection for ion \( i \) to get the collision with ion \( k \) at \( t_k \). For the whole system, the redo may greatly lower the efficiency, since near boundaries, ion collisions happen frequently.

To improve the efficiency, we keep all the potential collisions for each ion in a list, so we don’t need to redo the detection if the “impending” collision is “invalidated”. The potential collision list will also be sorted in the order of collision times. In this list, the first collision will be marked “active” and be inserted into the “Priority Queue”, while the rest will be marked “void” and will not be inserted to the “Priority Queue” unless the previous “active” one is found to be “invalidated” and ignored.

Maintenance after each collision.

When collision happens between ions, all the possible collisions associated with these two ions will be marked “invalidated”, and a new detection is conducted for these two ions. What about the ions in the “invalidated” collisions? Some maintenance has to be done.

Consider the following case: ion \( i \) has two possible collisions, with ion \( q_1 \) at time \( t_1 \), with ion \( j \) at time \( t_{ij} \), and \( t_1 < t_{ij} \); ion \( j \) also has two possible collisions, with ion \( q_2 \) at time \( t_2 \), with ion \( i \) at time \( t_{ij} \), and \( t_2 < t_{ij} \). If ion \( q_1 \) has collision before \( t_1 \) and ion \( q_2 \) has collision before \( t_2 \), the collision at time \( t_1 \) between ion \( i \) and \( q_1 \) and the collision at time \( t_2 \) between ion \( j \) and \( q_2 \) will be marked “invalidated”, and collision between ion \( i \) and \( j \) at time \( t_{ij} \) should be activated, and inserted to the “Priority Queue”.

So, after each collision, the routines are as follows:

1. mark as “invalidated” all the collisions of the two ions,
2. detect new collisions for the two ions and construct their new collision lists,

3. update the collision lists of all the ions associated with the new marked “invalidated” collisions, activate their first potential collision and insert into the “Priority Queue”.

To detect collisions for each ion, neighboring ions are searched. A “Neighbor List” is used on the basis of the “Cell List” used in SPME algorithm.

This approach proves to be robust and accurate in modeling the steric effects in simulations, and results are discussed in Sec. 4.3.3.
In this chapter we will first illustrate the results of the algorithm for the confined Stokes flow. One point force induced flow and multi random forces induced flow will be shown. And the convergence of the method will be discussed.

Then we will show the simulation results for electrokinetics. The simulation domain is a box of unit length, periodic in $x$ and $y$ direction. A reflection method is used when the ions move out of the box in the $z$ direction. The results for the charge density distribution resulted from Langevin approach will be shown, and will be compared with continuum theory. Using the Stokes solver just developed, we will also simulate electro-osmotic flow and compare the flow profile with the continuum theory.
4.1 Confined Stokes Flow Field

Figure 4.1: Force near wall (a) xz plane of x force (b) xy plane of x force (c) xz plane of z force (d) xy plane of z force.

Fig. 4.1 shows the flow field induced by one point force located at 3/32 away from the wall. We can see that the no-slip boundary condition is satisfied. And near the wall, the flow gradient is very large, which is a consequence of the singularity.

See Fig. 4.2, Fig. 4.3 and Fig. 4.4 for streamlines of 4, 10 and 50 random forces, respectively, randomly distributed in the domain. It can also be seen that the no-slip boundary conditions are enforced. Some of the streamlines are not closed, this is because all the forces are distributed in the 3D domain, but the streamlines are just a 2D slice of the flow field. The unclosed streamlines means the flow outwards the plane.
Figure 4.2: 4 random forces (a) \(xz\) plane of case 1 (b) \(xy\) plane of case 1 (c) \(xz\) plane of case 2 (d) \(xy\) plane of case 2.
Figure 4.3: 10 random forces (a) $xz$ plane of case 1 (b) $xy$ plane of case 1 (c) $xz$ plane of case 2 (d) $xy$ plane of case 2.
Figure 4.4: 50 random forces (a) $xz$ plane of case 1 (b) $xy$ plane of case 1 (c) $xz$ plane of case 2 (d) $xy$ plane of case 2.
4.1.1 Image System Effects

In this section, we discuss how the image system contributes to the improvement of the “Boundary Correction”. If we only consider the image system and “Boundary Correction”, see Fig. 4.5, the governing equations are simply the homogeneous Stokes equations inside the domain, with no forces and no-slip boundary conditions. Clearly the solution is zero.

\[-\nabla^2 \mathbf{u} + \nabla p = 0
\]
\[\nabla \cdot \mathbf{u} = 0
\]
\[\mathbf{u} = 0
\]

Figure 4.5: Image system + “Boundary Correction”.

How does this improve the accuracy of the “Boundary Correction”, since the “Boundary Correction” will give zero net flow to the solution? Consider the case of a point force very close to the wall. A large number of Fourier modes is required to give an accurate description of the flow on the boundary due to the large flow gradient near the singular point. When the number of Fourier modes is finite, the error might be big. However, when the image system is added, the flow of point force and its image system nearly negate each other, so that the gradient will be much smaller and a relatively smaller number of Fourier modes can be used to represent the boundary flow to high accuracy. In other words, with finite number of Fourier modes, the accuracy of the “Boundary Correction” is increased.

See Fig. 4.6 and Fig. 4.7 for a comparison of the wall flow velocity magnitude spectrum of one point force near the wall, with and without the image
system. The direction of the force is along the wall and normal to the wall respectively.

From the spectra in Fig. 4.6 and Fig. 4.7, we can see that in the low wave number range, the magnitude of the flow is much smaller, and the decay of flow velocity with wave number is also faster. The faster decay is more obvious in the $z$ force case. While from the contours we can see the big flow gradient on the left without image system, and the flow is nearly zero on the right, which is a result of the image system. Hence if a finite number of Fourier modes is used for the “Boundary Correction”, the accuracy will be better if the image system is included.
Figure 4.7: Wall flow velocity magnitude spectrum, $z$ force.
4.1.2 Cut Off Distance for Image System

When there are more than one point force, the above conclusion still applies due to the linearity of Stokes flow. A natural question arises: does adding more images keep improving the solution? The answer is no. Because given the padding length, when increasing the cutoff for images, more point forces away from the walls will be included. In this case, their images become very close to the other boundary of the simulation domain due to the periodicity of the simulation domain, hence having an effect on the wall on the other side. Also note that the strength of the image increases with the square of the distance from the wall, so that the effect on the other wall becomes big if the point force is not very close to the wall. As a result, the performance of the “Boundary Correction” method is not necessarily improved when more point forces far from the wall are included.

To illustrate this, averaged spectra for different values of image system cutoff distance are compared. The simulations are run with 512 randomly distributed point forces averaged over 100 simulations, with the cutoff for SPME being 0.2, the padding size of the domain being the same as SPME. In Fig. 4.8, we can see the decay of the averaged flow velocity with wave number. When the cutoff for images is about 0.12, the steepest decay of flow spectrum is achieved.

Another comparison of different cutoffs in SPME (also the padding length) is also plotted in Fig. 4.9. We can see the slope of the spectrum at low wave numbers. It can be seen the biggest decay mostly occurs around 60% to 80% of the padding.

On the other hand, if we increase the padding length, the images will be further from the other wall, so as to have a weaker effect on the other side. However, a very large padding also lowers the resolution of SPME in Fourier space, so the padding length should not be set too large for optimal performance.
Figure 4.8: Average wall flow velocity magnitude spectrum.

Figure 4.9: Slope of average wall flow velocity magnitude spectrum.
4.2 Convergence

To test the convergence of SPME and the “Boundary Correction” method versus the number of Fourier modes in both cases, we compare the results with an analytical Green’s function in a doubly-periodic domain.

4.2.1 Green’s Function for 2D Periodic Stokes

The detailed derivation of the 2D periodic Stokes Green’s function is given in Appendix C. Here we will list the outline.

Expand the field \( u = f(u, v, w)^T \), and pressure \( P \) in Fourier series, periodic in the \( x \) and \( y \) directions:

\[
\begin{align*}
  u &= \sum_{k_x, k_y} \hat{u}(z)e^{i(k_x x + k_y y)}, \\
  v &= \sum_{k_x, k_y} \hat{v}(z)e^{i(k_x x + k_y y)}, \\
  w &= \sum_{k_x, k_y} \hat{w}(z)e^{i(k_x x + k_y y)}, \\
  P &= \sum_{k_x, k_y} \hat{P}(z)e^{i(k_x x + k_y y)}
\end{align*}
\]

where \( k_x = 2\pi \cdot l, \quad k_y = 2\pi \cdot m, \quad l, m = ... -2, -1, 0, 1, 2... \)

Defining \( k = \sqrt{k_x^2 + k_y^2} \), the Fourier coefficients are given as follows on both sides of the point force, respectively.

On one side:

\[
\begin{align*}
  \hat{u}_L &= A_1 \sinh(kz) + \frac{k_x}{k}z[C_L \cosh(kz) + B_L \sinh(kz)], \\
  \hat{v}_L &= A_2 \sinh(kz) + \frac{k_y}{k}z[C_L \cosh(kz) + B_L \sinh(kz)], \\
  \hat{w}_L &= A_3 \sinh(kz) + z[B_L \cosh(kz) + C_L \sinh(kz)], \\
  \hat{P}_L &= 2[B_L \cosh(kz) + C_L \sinh(kz)],
\end{align*}
\]

where \( B_L = -kA_3 \) and \( C_L = -i(k_x A_1 + k_y A_2) \).

45
On the other side, we have

\[
\hat{u}_R = A_4 \sinh(kz') + i \frac{k_x}{k} z' [C_R \cosh(kz') + B_R \sinh(kz')],
\]

\[
\hat{v}_R = A_5 \sinh(kz') + i \frac{k_y}{k} z' [C_R \cosh(kz') + B_R \sinh(kz')],
\]

\[
\hat{w}_R = A_6 \sinh(kz') + z' [B_R \cosh(kz') + C_R \sinh(kz')],
\]

\[
\hat{P}_R = 2 [B_R \cosh(kz') + C_R \sinh(kz')],
\]

(4.3)

where \( z' = L - z \), \( B_R = -kA_6 \) and \( C_R = -i(k_x A_4 + k_y A_5) \).

When the force is normal to the wall, or in the \( z \) direction, the jump condition is \( [\hat{P}] = 1 \), while \( \hat{u}, \hat{v}, \hat{w}, \hat{u}_z, \hat{v}_z, \hat{w}_z \) are continuous across the jump. Using these conditions to solve for the \( A_i \) we can get:

\[
A_1 = -i k_x \frac{z \sinh(kL) \sinh(kL - k z) - kL(L - z) \sinh(k z)}{k [1 + 2k^2 L^2 - \cosh(2kL)]},
\]

(4.4a)

\[
A_2 = -i k_y \frac{z \sinh(kL) \sinh(kL - k z) - kL(L - z) \sinh(k z)}{k [1 + 2k^2 L^2 - \cosh(2kL)]},
\]

(4.4b)

\[
A_3 = \frac{[1 + 2k^2 L(L - z)] \cosh(k z) - \cosh(2kL - k z)}{2k [1 + 2k^2 L^2 - \cosh(2kL)]}
+ \frac{(2L - z) \sinh(k z) - z \sinh(2kL - k z)}{2 [1 + 2k^2 L^2 - \cosh(2kL)]},
\]

(4.4c)

\[
A_4 = i k_x \frac{(L - z) \sinh(kL) \sinh(k z) - kLz \sinh(kL - k z)}{k [1 + 2k^2 L^2 - \cosh(2kL)]},
\]

(4.4d)

\[
A_5 = i k_y \frac{(L - z) \sinh(kL) \sinh(k z) - kLz \sinh(kL - k z)}{k [1 + 2k^2 L^2 - \cosh(2kL)]},
\]

(4.4e)

\[
A_6 = \frac{(1 + 2k^2 Lz) \cosh(kL - k z) - \cosh(kL + k z)}{2k [1 + 2k^2 L^2 - \cosh(2kL)]}
+ \frac{(L + z) \sinh(kL - k z) - (L - z) \sinh(kL + k z)}{2 [1 + 2k^2 L^2 - \cosh(2kL)]},
\]

(4.4f)

When the force is along the wall, or in the \( z \) direction, the jump conditions are \( [\hat{P}_z] = i k_x \) and \( [\hat{u}_z] = -1 \), while \( \hat{u}, \hat{v}, \hat{w}, \hat{P}, \hat{v}_z, \hat{w}_z \) are continuous. Using
these conditions to solve for the $A_i$ we can get:

$$A_1 = \frac{1}{2k^3 \sinh(kL)(1 + 2k^2L^2 - \cosh(2kL))}\{-2k_y^2 \sinh^2(kL) \sinh(kL - kz)$$

$$+ k k_x^2 \sinh(kL)[z \sinh(2kL - kz) - (2L - z) \sinh(kz)]$$

$$+ k^2 [2(k_y^2 L^2 - k_x^2 Lz) \cosh(kz) \sinh(kL)$$

$$- 4k_y^2 L^2 \cosh(kL) \sinh(kz) - 2 \sinh^2(kL) \sinh(kL - kz)]$$

$$+ 2k^4 L^2 \cosh(kz) \sinh(kL)\},$$

(4.5a)

$$A_2 = \frac{k_x k_y}{2k^3 \sinh(kL)(1 + 2k^2L^2 - \cosh(2kL))}\{2 \sinh^2(kL) \sinh(kL - kz)$$

$$+ k \sinh(kL)[z \sinh(2kL - kz) - (2L - z) \sinh(kz)]$$

$$- 2k^2 L[(L + z) \cosh(kz) \sinh(kL) - 2L \cosh(kL) \sinh(kz)]\},$$

(4.5b)

$$A_3 = -ik_x \frac{kL(L - z) \sinh(kz) + z \sinh(kL) \sinh(kL - kz)}{k[1 + 2k^2L^2 - \cosh(2kL)]},$$

(4.5c)

$$A_4 = \frac{1}{2k^3 \sinh(kL)(1 + 2k^2L^2 - \cosh(2kL))}\{-2k_y^2 \sinh^2(kL) \sinh(kL)$$

$$+ k k_x^2 \sinh(kL) [(L - z) \sinh(kL + kz) - (L + z) \sinh(kL - kz)]$$

$$+ k^2 [2(k_y^2 L^2 - k_x^2 Lz) \cosh(kL - kz) \sinh(kL)$$

$$- 4k_y^2 L^2 \cosh(kL) \sinh(kL - kz) - 2 \sinh^2(kL) \sinh(kz)]$$

$$+ 2k^4 L^2 \cosh(kL - kz) \sinh(kL)\},$$

(4.5d)

$$A_5 = \frac{k_x k_y}{2k^3 \sinh(kL)(1 + 2k^2L^2 - \cosh(2kL))}\{2 \sinh^2(kL) \sinh(kz)$$

$$+ k \sinh(kL)[(L - z) \sinh(kL + kz) - (L + z) \sinh(kL - kz)]$$

$$- 2k^2 L[(2L - z) \cosh(kL - kz) \sinh(kL) - 2L \cosh(kL) \sinh(kL - kz)]\},$$

(4.5e)

$$A_6 = ik_x \frac{kLz \sinh(kL - kz) + (L - z) \sinh(kL) \sinh(kz)}{2k[1 + 2k^2L^2 - \cosh(2kL)]}. $$

(4.5f)

To test convergence, 64 Fourier modes for The Green’s function are used for comparison. It should be pointed out that near the singularity, an infinite number of Fourier modes is required to model the high gradient of the flow field. In this region, the Green’s function cannot converge to the exact solution due to the truncation of the Fourier modes.

It should also be noted that the jump conditions of the $x$ and $z$ force are different. When the force is along the wall, the discontinuity lies in the derivative of pressure and velocity; when the force is normal to the wall,
the discontinuity lies in pressure. The different jump conditions make the solutions exhibit different smoothness, and we expect smoother behavior for the $x$ force than for the $z$ force. And it is anticipated that Green’s function converge better for smoother functions, so we expect that when the force is along the wall, the Green’s function is more accurate.

In the convergence study, the velocity is calculated on 16 uniformly distributed grid points along each direction. The RMS error is calculated on these grid points according to

$$\frac{\|u - u_0\|^2}{\|u_0\|^2};$$

(4.6)

where $u$ denotes the velocity computed in our method, while $u_0$ denotes the flow calculated using the analytical Green’s function.

4.2.2 SPME Convergence

64 modes for the “Boundary Correction” method are used, which ensures its convergence as shown in the next section, and the number of SPME varied from 2 to 64. The convergence of SPME versus number Fourier modes can be seen in Fig. 4.10. Due to the error in the Green’s function in the area near the singularity, the near field is excluded in addition to the comparison of the whole domain.

In Fig. 4.10, we can see that for the $x$ force, when 32 Fourier modes are used, SPME produces very accurate results, and 64 modes make the error almost approach machine precision. Exclusion of the near field makes the error even smaller. For the $z$ force, the error is larger than for the $x$ force, which is a consequence of the different smoothness of Green’s function.

4.2.3 “Boundary Correction” Convergence

64 modes for SPME are used, which ensures full convergence of SPME as shown above, and the number of modes for the “Boundary Correction” method varied from 2 to 64. The convergence of the “Boundary Correction” versus number of Fourier modes can be seen in Fig. 4.11. Three cases are compared: (1).unit simulation domain without padding; (2).simulation
domain with padding, but without image; (3). with images.

In Fig. 4.11, we can see that for the $x$ force, when 16 Fourier modes are used, the “Boundary Correction” has almost converged with the image system. It converges more slowly without the image system. And without the padding, the unit simulation domain does not converge as well as in the other cases. The same conclusion holds for the $z$ force. Due to the different smoothness of Green’s function, error in the $z$ force case is slightly larger than for the $x$ force.

Figure 4.10: SPME convergence.
Figure 4.11: “Boundary Correction” convergence.
4.3 Steady State Charge Density

From this section, we will show the results for the charge density using the Langevin approach, and compared with the continuum theory. First the steady state charge density for imposed electrical potential and charged wall will be shown, followed by the steric effects on the charge density. In the subsequent sections, the transient charging process as well as the simulations for multi species will also be discussed. Finally, the electro-osmotic flow simulation will be shown.

4.3.1 Imposed Electrical Potential

Fig. 4.12 shows the steady state charge density with an imposed wall potential. The Langevin simulation is run with 512 ions, \( V = 8, \frac{\lambda D}{k} = 0.6 \). A finite volume method is used to solve for the charge density in the PNP equations.

![Charge density plot](image)

Figure 4.12: Charge density of imposed potential.

From Fig. 4.12, we can see that the steady state charge density is well modeled by the Langevin approach.
4.3.2 Charged Wall

Fig. 4.13 shows the steady state charge density in the case of charged wall. A single species of negative ions and two species of both negative and positive ions are both simulated. The first case is run with 1024 negative ions inside the domain, and 1024 fixed positive ions on the wall to represent the wall charge. We set $\frac{\lambda_D}{L} = 0.3$. The second case is run with 1000 ions inside the domain, and 400 fixed positive ions on the wall to represent the wall charge. Inside the domain, there are 700 negative ions and 300 positive ions, so that the total charge is zero. We set $\frac{\lambda_D}{L} = 0.2$.

![Figure 4.13: Charge density of charged wall (a) negative ion only (b) both negative and positive ion.](image)

From Fig. 4.12, we can see that the steady state charge density is also well modeled for charged walls. The charge density of each species is accurately captured.

4.3.3 Steric Effects on the Charge Density

If the finite size of ions is taken into account using the contact algorithm discussed before in Sec. 3.5, we obtain the charge density shown in Fig. 4.14. The simulation is run with $26^3 = 17576$ ions, $V = 8$, $\lambda_D/L = 0.2$, and ion radius is 0.016, corresponding to $\nu_a = 0.57593$ in the MPB theory.

From Fig. 4.14, we can see near the wall, several layers of ions are formed, which is a direct consequence of finite size of ions. This is a feature that continuum model can not capture due to the continuum assumption. However,
in the center portion of the domain, the charge density agrees very well with the MPB theory.

### 4.4 Transient of Charge Density

The transient evolution of the charge density is compared in this section. First we look at the case without steric effects. The Langevin simulation is run with 1000 ions, $V = 6$, $\lambda_D^3 = 0.3$. A finite volume method is used to calculate the evolution of charge density in the PNP equations. See Fig. 4.15 for the results.

From Fig. 4.15, we see that at different times, the charge densities are all well captured. And the evolution of charge density becomes slower as the density approaches steady state. At dimensionless time of 0.4, it is very close to steady state.

If we include the steric effects, and compare with evolving MPB equation, we can get the transient process of charge density with steric effects. The simulation is run with $26^3 = 17576$ ions, $V = 6$, $\lambda_D^3/L = 0.3$, and ion radius $0.042$, corresponding to $\nu_a = 0.57593$ in MPB theory. See Fig. 4.16 for the
results.

From Fig. 4.16, we see that at different time, the charge densities with steric effects are all also well captured. At dimensionless time of 0.4, it also evolves closely to steady state.

### 4.4.1 Multi Diffusivity

When we consider different kinds of species with different diffusivities, as described by Eqn. (2.19) and Eqn. (2.20), we can obtain an asymmetric evolution. Consider diffusivities of 1 and 0.2, and the Langevin simulation is run with 1000 ions, $V = 6$, $\frac{\lambda_D}{L} = 0.3$. See Fig. 4.17 for the results.

From Fig. 4.17, we see that different diffusivities change the evolving speed of each species, which breaks the symmetry of the transient process. However the steady state remains the same. This conclusion confirms the previous analysis in Sec. 2.3.
Figure 4.16: Transient process of charge density with steric effects.

Figure 4.17: Transient process of charge density for multi diffusivity.
4.4.2 Multi Valences

When we consider different kinds of species with different valences, as described by Eqn. (2.19) and Eqn. (2.20), we also observe an asymmetric evolution as well as an asymmetric steady state. Consider valences of 2 and -2/3, and the Langevin simulation is run with 1000 ions, with 250 positive ions and 750 negative ions, and the total charge remains zero. \( V = 6, \frac{\lambda_P}{D} = 0.3 \). See Fig. 4.18 for the results.

Figure 4.18: Transient process of charge density for multi valences.

From Fig. 4.18, we see that the symmetry is broken for both transient and steady state. A higher valence resulted in a higher charge density on one side. This conclusion also confirms the previous analysis in Sec. 2.3.

4.5 Simulating Electro-Osmotic Flow

The velocity profile predicted by the continuum approach can be obtained from the Stokes equations Eqn. (2.21). As discussed in Sec. 2.4.1, the velocity profile and electrical potential should adopt the same shape. Using the method discussed in Sec. 2.4.2, we can apply the confined Stokes solver
developed in Sec. 3.3 to simulate the electro-osmosis phenomenon.

The Langevin simulation is run with 1024 negative ions inside the domain, and 1024 fixed positive ions on the wall to represent the wall charge. \( V = 6, \frac{\lambda \rho}{T} = 0.3 \). See Fig. 4.19 for the results. From Fig. 4.19, we see that the velocity profile is also well modeled, with a good match with the potential profile.
CHAPTER 5
CONCLUSION, APPLICATION AND FUTURE WORK

5.1 Summary and Conclusion

We have proposed a novel way to model electrochemical transport and diffuse charge dynamics phenomena using a Langevin equation.

First, we have tested the equivalence of the continuum PNP equations and the discrete Langevin formulation developed in Chap. 2, and the cases we tested included:

- steady state of charge density for symmetric binary electrolyte with imposed wall potential and between charged walls
- dynamical transient process of symmetric binary electrolyte
- steady state and transient of multi species of different diffusivity and valence

An efficient SPME algorithm is used to calculate the electrical interactions between ions. The imposed wall potential is enforced by superimposing auxiliary electrical potential fields to match the boundary condition. The SPME method and boundary condition enforcement share the same spirit as the Stokes interactions discussed below. It is shown that the continuum theory and Langevin approach agree well in these scenarios.

Second, we also modeled the effect of steric interactions between ions, and compared the steady state and transient process with a modified Poisson-Boltzmann equation. The contact algorithm used for steric effects is based on an event driven idea. The algorithm treats the ions as hard spheres, and resolves the collisions between ions one by one in the order of happening times. The Langevin approach is in good agreement with MPB theory for the charge density away from the wall, and our simulations were also successful
at capturing steric effects near the wall, where the charge density can not exceed a certain limit, and provide some discrete features that the continuum MPB theory can not predict.

We have also implemented a fast algorithm, which can compute efficiently the Stokes hydrodynamic interactions between two confining walls in a doubly-periodic domain. This algorithm, based on a previously developed SPME method, enforces the no-slip boundary condition along the $z$ direction by superimposing a “Boundary Correction” negating the flow of SPME on the boundary. This method makes use of the periodicity in $x$ and $y$ direction by employing FFT to gain efficiency. In addition, an image system consisting of a point force, force dipole and mass dipole is also added to improve the convergence of the “Boundary Correction”. The computation involved with the image system can be handled using a generalized SPME method.

When applying the confined Stokes algorithm to the Langevin description of electrokinetic phenomena, our method allows us to simulate electro-osmotic flow, by treating each ion as point force. The resulting flow profile is in good agreement with continuum theory.

5.2 Potential Applications

The various methods developed in this work will be applicable to a wide range of engineering problems involving electrokinetic flows in highly confined geometries. Below, we outline three applications that might be investigated in the future.

*Electrochemical transport through nanocapillary array membranes.*

Nanocapillary array membranes, or NCAMs, are membranes made of microfabricated arrays of nanosized channels [7], and have recently found a wealth of applications in the field of microfluidics. Chemical transport through these membranes is quite unique owing to the very small size of the capillaries, in which the EDLs overlap and interact. One example of unusual properties that these membranes offer is permselectivity, by which ions of the same charge as those in the EDL are rejected, whereas counter-ions are transported [64]. This phenomena has driven a lot of interest in these membranes, which are now used
in a wide variety of microfluidic devices for functions such as chemical separation [65, 66], chemical analysis (using wall-tethered receptors such as antibodies or DNA probes) [67, 68], water purification [21, 22, 23], etc. Because of the high complexity of the physics of electrokinetic flows through NCAMs, continuum models based on the PNP equations are not able to capture these various phenomena. A number of molecular dynamics studies have been performed and are able to reproduce experimental observations, e.g. see [69, 70], but these still suffer from the very high cost of MD simulations. Here, we propose to apply the Langevin approach described above to study transport through NCAMs. We could first consider the simple transport of an electrolyte through a single nanocapillary, after which more complex situations could be studied, including the transport of macromolecules, and the kinetics of chemical analysis in NCAMs using wall-tethered probes. We expect the use of the Langevin method to be particularly useful in this last case, as macromolecular tethering occurs on a diffusive time-scale which is typically too long to simulate using MD.

**Polyelectrolyte transport in nanochannels.**

This application is motivated by the recent experiments by Pennathur et al. [62, 63, 13] involving the separation of DNA fragments (of a few base pairs in length) and oligonucleotides in nanochannels. DNA separation by electrophoresis is not possible in bulk solutions, as all the molecules have the same migration velocity irrespective of their length, a direct consequence of the Helmholtz-Smoluchowski formula (see Chap. 1). It is therefore typically achieved in gels [18], which are generally quite costly. Pennathur et al. however showed that when placed in nanochannels (with widths of the order of 100 nm), DNA fragments of different sizes migrate with different electrophoretic velocities. The precise mechanisms for this separation are not entirely clear to date, and must involve a subtle coupling between migration under the action of the applied field, transport by the (nonuniform) electro-osmotic flow, interactions with the overlapping EDLs on the channel walls, particle orientation, etc. Using the methods described in the previous sections, we could perform detailed simulations of this problem with the aim of elucidating the leading mechanisms resulting in separation. We could
first consider the case of rigid rod-like particles, which is an appropriate model for very short DNA fragments (of less than 150 base pairs, or one persistence length), and then investigate the effects of flexibility using more sophisticated models for polymer dynamics. Ultimately, these simulations could be used to determine the experimental conditions required to achieve optimal resolution in the separation process.

**Electrically driven polymer translocation through nanopores.**

The transport of polymeric molecules through nanosized pores, known as polymer translocation, plays an important role in a great number of biological or biophysical processes, e.g. [71, 72]. It has also been shown experimentally that polymer translocation, when applied to DNA, can be used to obtain information about the DNA secondary structure by measuring the accompanying ionic current [26]. Controlled DNA translocation may therefore be used as tool for genomic sequencing, suggesting the need for more detailed modeling of this process. The fundamental difference in the modeling of this problem with respect to polymer transport in a simple nanochannel has to do with the geometry of the system, in which the pore entrance and exit must be accounted for. This problem has previously been addressed using both analytical models based on the PNP equations [73, 74], and using coarse-grained Brownian dynamics simulations, e.g. [75, 76]. However, these previous modeling attempts all used a continuum description of the electrolyte, which may be inadequate in very thin pores where the diffuse charge dynamics may be significant. To include these effects, we also could apply the Langevin approach of Chap. 2. The complex geometry of the pore entrance and exit can be accounted for by extension of the method described in Sec. 3.3.2.

## 5.3 Future Work

Several possible Improvements to our algorithm are also listed below:

*complex geometries:*

The SPME and “Boundary Correction” method can be applied to more complicated geometries. Although in this work, simulations are solely
conducted in cubes, the same idea can be readily applied to different domains.

nonhomogeneous fluids:
When the fluid inside the domain is not homogeneous, for example, with varying viscosity, the “Boundary Correction” method may not hold. Sharing the same spirit, generalized method may be formulated to handle this case.

unsteady dynamics:
During unsteady charging of the surface, or in high-frequency alternating fields, all procedures may have to be repeated at each time step of the simulation. The physics behind these dynamics has yet to be explored.

alternative way to calculate fluid flow:
We could first obtain a smooth force distribution by extrapolation from the excess ion positions, from which the resulting fluid flow would be determined by solution of the Stokes equations including this body force.
APPENDIX A

EWALD SUM FORMULATION

A.1 Periodic Stokes Equation

\[ \nabla \cdot \mathbf{u} = 0, \quad \mu \nabla^2 \mathbf{u} = \nabla P + \mathbf{F} \sum_n \delta(\mathbf{r} - \mathbf{r}_n). \tag{A.1} \]

Expand \( \mathbf{u}, \ P \) in Fourier series:

\[ \mathbf{u} = \sum_k \mathbf{u}_k e^{-2\pi i (k \cdot \mathbf{r})}, \]

\[ -\nabla P = \sum_k \mathbf{P}_k e^{-2\pi i (k \cdot \mathbf{r})}, \]

\[ \sum_n \delta(\mathbf{r} - \mathbf{r}_n) = \frac{1}{\tau_0} \sum_k e^{-2\pi i k \cdot \mathbf{r}}, \tag{A.2} \]

where \( \tau_0 \) is the volume of unit cell.

A.1.1 \( \mathbf{k} \cdot \mathbf{P}_k \)

The curl of pressure is 0:

\[ \nabla \times (-\nabla P) = \sum_k \nabla \times (\mathbf{P}_k e^{-2\pi i (k \cdot \mathbf{r})}) = 0. \tag{A.3} \]

So

\[ \mathbf{k} \times \mathbf{P}_k = 0. \tag{A.4} \]

We must have

\[ \mathbf{P}_k = \frac{1}{k^2} (\mathbf{k} \cdot \mathbf{P}_k) \mathbf{k}. \tag{A.5} \]
\section*{A.1.2 $u_k$}

The orthogonality of Fourier modes gives:

$$-4\pi^2 \mu k^2 u_k = -P_k + \frac{F}{\tau_0}. \quad (A.6)$$

We can solve for $u_k$:

$$u_k = \frac{1}{4\pi^2 \mu k^2} \left( P_k - \frac{F}{\tau_0} \right). \quad (A.7)$$

Substitute (A.5) into the above, yielding:

$$u_k = \frac{1}{4\pi^2 \mu k^2} \left( \frac{1}{k^2} (k \cdot P_k) k - \frac{F}{\tau_0} \right). \quad (A.8)$$

\section*{A.2 Point Force}

Taking the inner product of (A.6) with $k$, for $k \neq 0$, gives:

$$k \cdot P_k = \frac{1}{\tau_0} k \cdot F. \quad (A.9)$$

Substituting into (A.8), the velocity is given by

$$u_k = \frac{1}{4\pi^2 \mu \tau_0} \left( \frac{(k \cdot F)k}{k^4} - \frac{F}{k^2} \right) \quad (k \neq 0) \quad (A.10)$$

Define

$$\sigma_1 = \sum_{k \neq 0} e^{-2\pi i (k \cdot r)} \frac{1}{k^2}, \quad (A.11a)$$

$$\sigma_2 = \sum_{k \neq 0} e^{-2\pi i (k \cdot r)} \frac{1}{k^4}, \quad (A.11b)$$

then the velocity can be written as

$$u = u_0 - \frac{1}{4\pi \mu} \left[ \frac{1}{\pi \tau_0} \sum_{k \neq 0} e^{-2\pi i (k \cdot r)} \frac{1}{k^2} + \nabla \left( \nabla \cdot \frac{1}{4\pi^3 \tau_0} \sum_{k \neq 0} e^{-2\pi i (k \cdot r)} \frac{1}{k^4} \right) \right] F$$

$$= u_0 - \frac{1}{4\pi \mu} \left[ \frac{1}{\pi \tau_0} \sigma_1 + \nabla \left( \nabla \cdot \frac{1}{4\pi^3 \tau_0} \sigma_2 \right) \right] F. \quad (A.12)$$

64
A.2.1 Ewald Summation Formula

We start with the following integral representation for $1/k^{2m}$, valid for any integer $m > 0$:

$$\frac{1}{k^{2m}} = \frac{\pi^m}{\Gamma(m)} \int_0^\infty e^{-\pi k^2 \beta} \beta^{m-1} \, d\beta, \quad (A.13)$$

where $\Gamma(m)$ is the complete $\Gamma$ function. When $m = 1$ we get:

$$\frac{1}{k^2} = \frac{\pi}{\Gamma(1)} \int_0^\infty e^{-\pi k^2 \beta} \, d\beta = \pi \int_0^\infty e^{-\pi k^2 \beta} \, d\beta. \quad (A.14)$$

Substitute into (A.11a)

$$\sigma_1 = \sum_k \frac{e^{-2\pi i (k \cdot r)}}{k^2}$$

$$= \pi \int_0^\infty \sum_k e^{-\pi k^2 \beta - 2\pi i (k \cdot r)} \, d\beta$$

$$= \pi \int_0^\infty \sum_k e^{-\pi k^2 \beta - 2\pi i (k \cdot r)} \, d\beta + \pi \int_\alpha^\infty \sum_k e^{-\pi k^2 \beta - 2\pi i (k \cdot r)} \, d\beta. \quad (A.15)$$

Then apply Ewald $\theta$-transformation formula:

$$\sum_k e^{-\pi k^2 \beta - 2\pi i (k \cdot r)} = \frac{\tau_0}{\beta^2} \sum_n e^{-\pi \frac{(r-r_n)^2}{\beta^2}}, \quad (A.16)$$

we can get:

$$\sigma_1 = \pi \int_0^\alpha \frac{\tau_0}{\beta^2} \sum_n e^{-\pi \frac{(r-r_n)^2}{\beta^2}} - 1 \, d\beta + \pi \int_\alpha^\infty \sum_k e^{-\pi k^2 \beta - 2\pi i (k \cdot r)} \, d\beta, \quad (A.17)$$

where the $-1$ in the first integral comes from the term $k = 0$ in the sums.

A.2.2 Point Force: Real Sum and Fourier Sum

Change variables to $\xi = \frac{\alpha}{\beta}$, so

$$d\xi = -\frac{\alpha}{\beta} d\beta, \quad d\beta = -\frac{1}{\alpha} \left(\frac{\alpha}{\beta}\right)^2 d\xi = -\frac{\alpha}{\xi^2} d\xi. \quad (A.18)$$
The first integral becomes:

\[
\pi \int_0^1 \frac{\tau_0}{\beta^2} \sum_n e^{-\frac{(r-r_n)^2}{\beta^2}} - 1 \, d\beta
\]

\[
= \pi \tau_0 \int_1^\infty \left( \frac{\xi}{\alpha} \right)^{\frac{3}{2}} \sum_n e^{-\frac{(r-r_n)^2}{\alpha}} \left( -\frac{\alpha}{\xi^2} \right) \, d\xi - \pi \alpha
\]

\[
= \frac{\pi \tau_0}{\alpha^{\frac{3}{2}}} \int_1^\infty \sum_n e^{-\frac{(r-r_n)^2}{\alpha}} \xi^{-\frac{1}{2}} \, d\xi - \pi \alpha. \quad (A.19)
\]

This part converges exponentially in real space, we call it real sum.

Change variables to \( \xi = \frac{\beta}{\alpha} \), so \( d\xi = \frac{d\beta}{\alpha} \). The second integral becomes:

\[
\pi \int_\alpha^\infty \sum_k e^{-\pi k^2 \beta - 2\pi i(k \cdot \mathbf{r})} \, d\beta = \alpha \pi \sum_k e^{-2\pi i(k \cdot \mathbf{r})} \int_\alpha^\infty e^{-\pi k^2 \alpha} \, d\xi
\]

\[
= \alpha \pi \sum_k e^{-2\pi i(k \cdot \mathbf{r})} \psi_0(\pi k^2 \alpha). \quad (A.20)
\]

This part converges exponentially in Fourier space, we call it Fourier sum.

Introducing the special function \( \psi_\nu(x) = \int_1^\infty \xi^\nu e^{-x \xi} d\xi \) and denoting \((\mathbf{r} - \mathbf{r}_n)^2\) as \( r^2 \), \( \sigma_1 \) simplifies to:

\[
\sigma_1 = \frac{\pi \tau_0}{\alpha^{\frac{3}{2}}} \sum_n \psi_{-\frac{1}{2}} \left( \frac{r^2}{\alpha} \right) - \pi \alpha + \pi \alpha \sum_k e^{-2\pi i(k \cdot \mathbf{r})} \psi_0(\pi k^2 \alpha). \quad (A.21)
\]

Similarly, we get \( \sigma_2 \):

\[
\sigma_2 = \pi^{\frac{1}{2}} \frac{\alpha}{\tau_0} \sum_n \psi_{-\frac{1}{2}} \left( \frac{r^2}{\alpha} \right) - \frac{\pi^2 \alpha^2}{2} + \pi^2 \alpha^2 \sum_k e^{-2\pi i(k \cdot \mathbf{r})} \psi_1(\pi k^2 \alpha). \quad (A.22)
\]

Substituting \( \sigma_1 \) and \( \sigma_2 \) into Eqn. (A.12), omitting the constant term, we get the real sum:

\[
- \frac{1}{4\pi \mu} \left[ \frac{1}{\alpha^{\frac{1}{2}}} \sum_n \psi_{-\frac{1}{2}} \left( \frac{r^2}{\alpha} \right) + \nabla \left( \frac{\alpha^{\frac{1}{2}}}{4\pi \tau_0} \sum_n \psi_{-\frac{3}{2}} \left( \frac{r^2}{\alpha} \right) \right) \right] \mathbf{F}
\]

\[
= \left[ \frac{\pi}{\alpha^2} \psi_{-\frac{1}{2}} \left( \frac{r^2}{\alpha} \right) (\mathbf{r}^2 \mathbf{I} + \mathbf{x} \otimes \mathbf{x}) - \frac{2}{\alpha^2} e^{-\frac{r^2}{\alpha}} \right] \mathbf{F}, \quad (A.23)
\]

66
as well as the Fourier sum:

\[- \frac{1}{4\pi\mu} \sum_k \sum \alpha^{2i\pi}\left[ \frac{\alpha}{\tau_0} \psi_0(\pi k^2 \alpha) + \nabla \left( \frac{\alpha^2}{4\pi\tau_0} \psi_1(\pi k^2 \alpha) \right) \right] \tilde{F}(\mathbf{k}) \]

\[= \sum_{k \neq 0} e^{-2\pi ik \cdot \mathbf{x}_m} \frac{\pi \alpha^2}{\tau_0} \psi_1(\pi \alpha k^2)(k^2 \mathbf{I} - \mathbf{k} \otimes \mathbf{k}) \tilde{F}(\mathbf{k}). \quad (A.24)\]

### A.2.3 Point Force Summary

Finally, we can write the velocity as

\[u(\mathbf{x}_m) = \sum_{\mathbf{p}} \sum_{n=1}^N A_F(\alpha, \mathbf{x}_m - \mathbf{x}_n + \mathbf{p}) F_{\mathbf{p}} + \sum_{k \neq 0} e^{-2\pi ik \cdot \mathbf{x}_m} B_F(\alpha, \mathbf{k}) \tilde{F}(\mathbf{k}). \quad (A.25)\]

The two second order tensors \( A_F \) and \( B_F \) are given by

\[A_F(\alpha, \mathbf{x}) = \frac{\pi}{\alpha^2} \psi_\frac{1}{2} \left( \frac{\pi r^2}{\alpha} \right) \left( r^2 \mathbf{I} + \mathbf{x} \otimes \mathbf{x} \right) - \frac{2}{\alpha^2} e^{-\frac{r^2}{\alpha}} \mathbf{I}, \quad (A.26)\]

\[B_F(\alpha, \mathbf{k}) = \frac{\pi \alpha^2}{\tau_0} \psi_1(\pi \alpha k^2)(k^2 \mathbf{I} - \mathbf{k} \otimes \mathbf{k}), \quad (A.27)\]

where \( r^2 = \|\mathbf{x}\|^2 \), and the functions \( \psi_\nu \) are special functions given by

\[\psi_\frac{1}{2}(x) = \frac{e^{-x}}{x} + \frac{\sqrt{\pi}}{2x^{\frac{1}{2}}} \text{erfc}(x), \quad \psi_1(x) = \frac{e^{-x}}{x^2}(1 + x). \quad (A.28)\]

### A.3 Force Dipole

The flow induced by a force dipole can be obtained by taking the limit of two opposite forces. From (A.2), we have

\[\mu \nabla^2 \left( \sum_k u_k e^{-2\pi ik \cdot \mathbf{r}} \right) \]

\[= - \sum_k P_k e^{-2\pi ik \cdot \mathbf{r}} + \frac{1}{\tau_0} \mathbf{F} \lim_{d \to 0} \sum_k \left( e^{-2\pi ik \cdot (\mathbf{r} - \mathbf{d})} - e^{-2\pi ik \cdot \mathbf{r}} \right) \]

\[= - \sum_k P_k e^{-2\pi ik \cdot \mathbf{r}} - \frac{1}{\tau_0} \mathbf{F} \sum_k \mathbf{d} \cdot (-2\pi i \mathbf{k}) \cdot e^{-2\pi ik \cdot \mathbf{r}}. \quad (A.29)\]
Let $\mathbf{F} \otimes \mathbf{d}$ be a constant 2nd order tensor $\mathbf{Fd}$:

$$\mu \nabla^2 \left( \sum_k u_k e^{-2\pi i k \cdot r} \right) = -\sum_k P_k e^{-2\pi i k \cdot r} + \frac{2\pi i}{\tau_0} \mathbf{Fd} \cdot \sum_k k \cdot e^{-2\pi i k \cdot r}. \quad (A.30)$$

So the dimensionless velocity due to a force dipole can be calculated by taking the gradient of the point force case (A.25):

$$u(x_m) = \sum_p \sum_{n=1}^N \frac{\partial}{\partial x_m} A_F(\alpha, x_m - x_n + p) \mathbf{Fd}_n$$

$$+ \sum_{k \neq 0} \frac{\partial}{\partial x_m} e^{-2\pi i k \cdot x_m} B_F(\alpha, k) \mathbf{Fd}(k)$$

$$= \sum_p \sum_{n=1}^N \frac{\pi}{\alpha^2} \frac{\psi_1}{\psi_1^2} \left( \frac{\pi r^2}{\alpha} \right) \left( -x - \frac{3x \otimes x \otimes x}{r^2} \right)$$

$$- 2\pi e^{\frac{-\pi^2}{\alpha^2}} \left( \frac{x \otimes x \otimes x}{r^2} - x \right)\mathbf{Fd}_n$$

$$+ \sum_p \sum_{n=1}^N \frac{\pi}{\alpha^2} \frac{\psi_1}{\psi_1^2} \left( \frac{\pi r^2}{\alpha} \right) \left[ x \cdot \mathbf{Fd}_n' + \text{Tr}(\mathbf{Fd}_n) \right]$$

$$- \sum_{k \neq 0} e^{-2\pi i k \cdot x_m} \frac{2\pi^2 \alpha^2}{\tau_0} \psi_1(\pi \alpha k^2)(k^2 k - k \otimes k \otimes k) \mathbf{Fd}(k), \quad (A.31)$$

which can also be written as

$$u(x_m) = \sum_p \sum_{n=1}^N A_{Fd}(\alpha, x_m - x_n + p) \mathbf{Fd}_n$$

$$+ \sum_{k \neq 0} e^{-2\pi i k \cdot x_m} B_{Fd}(\alpha, k) \mathbf{Fd}(k). \quad (A.32)$$

The two third order tensors $A_{Fd}$ and $B_{Fd}$ are given in index notation by

$$A_{Fdijk}(\alpha, x) = \frac{\pi}{\alpha^2} \frac{\psi_1}{\psi_1^2} \left( \frac{\pi r^2}{\alpha} \right) \left( -x_k \delta_{ij} - \frac{3x_i x_j x_k}{r^2} + x_j \delta_{ik} + x_i \delta_{jk} \right)$$

$$- 2\pi e^{\frac{-\pi^2}{\alpha^2}} \left( \frac{x_i x_j x_k}{r^2} - x_k \delta_{ij} \right), \quad (A.33)$$

$$B_{Fdijk}(\alpha, k) = -\frac{2\pi^2 \alpha^2}{\tau_0} \psi_1(\pi \alpha k^2)(k^2 k \delta_{ij} - k_i k_j k_k), \quad (A.34)$$
where the functions $\psi_{\nu}$ are special functions given by

$$
\psi_\frac{3}{2}(x) = \frac{e^{-x}}{x} + \frac{\sqrt{\pi}}{2x^\frac{3}{2}} \text{erfc} \sqrt{x}, \quad \psi_1(x) = \frac{e^{-x}}{x^2} (1 + x).
$$  \hspace{1cm} (A.35)

A.4 Mass Dipole

A.4.1 Conservation of Mass

Introducing a mass dipole, the mass conservation equation becomes:

$$
\nabla \cdot \mathbf{u} + \lim_{d \to 0} M \left[ \delta(\mathbf{r} - (\mathbf{r}_n - d)) - \delta(\mathbf{r} - \mathbf{r}_n) \right] = 0.
$$  \hspace{1cm} (A.36)

So

$$
\nabla \cdot \sum_k \mathbf{u}_k e^{-2\pi i (k \cdot \mathbf{r})} + \lim_{d \to 0} M \sum_k \left[ e^{-2\pi i (k \cdot (\mathbf{r} - d))} - e^{-2\pi i (k \cdot \mathbf{r})} \right] = 0.
$$  \hspace{1cm} (A.37)

Let $M \cdot \mathbf{d}$ be a constant vector $\mathbf{M} \mathbf{d}$, the above becomes:

$$
-2\pi i \sum_k k \cdot \mathbf{u}_k e^{-2\pi i (k \cdot \mathbf{r})} - \frac{1}{\tau_0} \sum_k \mathbf{M} \mathbf{d} \cdot (-2\pi i) ke^{-2\pi i (k \cdot \mathbf{r})} = 0.
$$  \hspace{1cm} (A.38)

So

$$
k \cdot \mathbf{u}_k = \frac{\mathbf{M} \mathbf{d}}{\tau_0} \cdot \mathbf{k}.
$$  \hspace{1cm} (A.39)

A.4.2 Flow Field Due to Mass Dipole

Without external force, Stokes equation becomes:

$$
4\pi^2 \mu k^2 \mathbf{u}_k = \mathbf{P}_k.
$$  \hspace{1cm} (A.40)

Take the inner product of the above with $\mathbf{k}$:

$$
4\pi^2 \mu k^2 (\mathbf{k} \cdot \mathbf{u}_k) = \mathbf{k} \cdot \mathbf{P}_k.
$$  \hspace{1cm} (A.41)
From (A.39), we have
\[ k \cdot P_k = 4\pi^2 \mu k^2 \frac{Md}{\tau_0} \cdot k. \] (A.42)

Substitute the above into (A.8):
\[
\begin{align*}
\mathbf{u}_k &= \frac{1}{4\pi^2 \mu k^2} \frac{1}{k^2} (k \cdot P_k) k \\
&= \frac{1}{4\pi^2 \mu k^2} \frac{1}{k^2} \left(4\pi^2 \mu k^2 \frac{Md}{\tau_0} \cdot k\right) k \\
&= \frac{1}{\tau_0} \frac{k \otimes k}{k^2} \cdot Md, \quad \text{(A.43)}
\end{align*}
\]

then the velocity becomes:
\[
\begin{align*}
\mathbf{u} &= \mathbf{u}_0 + \frac{1}{\tau_0} \sum_k \frac{e^{-2\pi i (k \cdot r)}}{k^2} (k \otimes k) \cdot Md \\
&= \mathbf{u}_0 - \frac{1}{4\pi^2 \tau_0} \nabla \left[ \nabla \cdot \left( \sum_k \frac{e^{-2\pi i (k \cdot r)}}{k^2} Md \right) \right] \\
&= \mathbf{u}_0 - \frac{1}{4\pi^2 \tau_0} \nabla \left[ \nabla \cdot (\sigma_1 Md) \right]. \quad \text{(A.44)}
\end{align*}
\]

A.4.3 Mass Dipole: Real Sum and Fourier Sum

Recall the expression for \( \sigma_1 \) in Eqn. (A.17), the real sum is given by
\[
\begin{align*}
&= -\frac{1}{4\pi^2 \tau_0} \nabla \left[ \nabla \cdot \left( \frac{\pi \tau_0}{\alpha^2} \sum_n \psi_{-\frac{1}{2}} \left( \frac{r^2}{\alpha} \right) - \pi \alpha \right) Md \right] \\
&= -\frac{1}{4\pi^2 \tau_0} \frac{\pi \tau_0}{\alpha^2} \frac{4\pi}{3\alpha} \left[ \frac{\pi}{\alpha \psi_{\frac{1}{2}}} \left( \frac{r^2}{\alpha} \right) \left( -r^2 \mathbf{I} + 3r \otimes r \right) - e^{-\pi \frac{r^2}{\alpha}} \mathbf{I} \right] \cdot Md \\
&= \frac{1}{3\alpha^2} \left[ \frac{\pi}{\alpha \psi_{\frac{1}{2}}} \left( \frac{r^2}{\alpha} \right) \left( r^2 \mathbf{I} - 3r \otimes r \right) - e^{-\pi \frac{r^2}{\alpha}} \mathbf{I} \right] \cdot Md \\
&= \left[ \frac{\pi}{3\alpha^2 \psi_{\frac{1}{2}}} \left( \frac{r^2}{\alpha} \right) \left( r^2 \mathbf{I} - 3r \otimes r \right) - \frac{1}{3\alpha^2} e^{-\pi \frac{r^2}{\alpha}} \mathbf{I} \right] \cdot Md, \quad \text{(A.45)}
\end{align*}
\]

where
\[
\psi_{\frac{1}{2}}(x) = \frac{e^{-x}}{x} + \frac{3}{2} \frac{e^{-x}}{x^2} + \frac{3\sqrt{\pi}}{4\alpha} \text{erfc}(\sqrt{x}). \quad \text{(A.46)}
\]
The Fourier sum is given by

\[- \frac{1}{4\pi^2\tau_0} \nabla \left[ \nabla \cdot \left( \alpha \pi \sum_{k} e^{-2\pi i(k\cdot r)} \psi_0(\pi k^2\alpha) \right) \hat{\mathbf{M}} \right] \]

\[= \frac{\alpha \pi}{\tau_0} \sum_{k} \left[ e^{-2\pi i(k\cdot r)} \psi_0(\pi k^2\alpha) \hat{k} \otimes \hat{k} \right] \cdot \hat{\mathbf{M}} \hat{\mathbf{d}}, \quad (A.47)\]

where

\[\psi_0(x) = \frac{e^{-x}}{x}. \quad (A.48)\]

A.4.4 Mass Dipole Summary

The flow velocity induced by a mass dipole is

\[u(x_m) = \sum_{p} \sum_{n=1}^{N} A_{Md}(\alpha, x_m - x_n + p) \hat{\mathbf{M}} \hat{\mathbf{d}}_n \]

\[+ \sum_{k \neq 0} e^{-2\pi i k \cdot x_m} B_{Md}(\alpha, k) \hat{\mathbf{M}} \hat{\mathbf{d}}(k). \quad (A.49)\]

The two second order tensors $A_{Md}$ and $B_{Md}$ are given by

\[A_{Md} = \frac{\pi}{3\alpha^{2}} \psi_{\frac{3}{2}} \left( \frac{r^2}{\alpha} \right) \left( r^2 \mathbf{I} - 3\hat{x} \otimes \hat{x} \right) - \frac{1}{3\alpha^{2}} e^{-\pi \frac{r^2}{2}} \mathbf{I}, \quad (A.50)\]

\[B_{Md} = \frac{\alpha \pi}{\tau_0} \psi_0(\pi k^2\alpha) \hat{k} \otimes \hat{k}, \quad (A.51)\]

where the functions $\psi_{\nu}$ are special functions given by

\[\psi_{\frac{3}{2}}(x) = \frac{e^{-x}}{x} + \frac{3}{2} \frac{e^{-x}}{x^2} + \frac{3\sqrt{\pi}}{4x^{\frac{3}{2}}} \text{erfc}(\sqrt{x}), \quad \psi_0(x) = \frac{e^{-x}}{x}. \quad (A.52)\]
APPENDIX B

THE “BOUNDARY CORRECTION”
METHOD FORMULATION

B.1 Arbitrary Boundary Condition (2 walls are different)

All Variables are dimensionless in the following derivation.
We are trying to solve the homogeneous Stokes equations:

\[-\nabla^2 u + \nabla P = 0,\]  \(\text{(B.1a)}\)

\[\nabla \cdot \mathbf{u} = 0,\]  \(\text{(B.1b)}\)

subject to boundary conditions:

\[u = u_1|_{(x,y,z=0)},\]  \(\text{(B.2a)}\)

\[u = u_2|_{(x,y,z=L)}.\]  \(\text{(B.2b)}\)

Expand the flow field \(\mathbf{u}\) and pressure \(P\) in Fourier series:

\[\mathbf{u} = \sum_{k_x} \sum_{k_y} \hat{\mathbf{u}}(k_x, k_y, z)e^{2\pi i (k_x x + k_y y)},\]  \(\text{(B.3a)}\)

\[P = \sum_{k_x} \sum_{k_y} \hat{P}(k_x, k_y, z)e^{2\pi i (k_x x + k_y y)}.\]  \(\text{(B.3b)}\)

Take the divergence of Eqn. (B.1):

\[\nabla \cdot \nabla^2 \mathbf{u} = \nabla^2 (\nabla \cdot \mathbf{u}) = \nabla \cdot \nabla P = \nabla^2 P = 0.\]  \(\text{(B.4)}\)

So

\[\nabla^2 P = 0.\]  \(\text{(B.5)}\)
Substitute Eqn. (B.3a) and Eqn. (B.3b) into Eqn. (B.5):

$$\nabla^2 P = \sum_{k_x} \sum_{k_y} [-4\pi^2 (k_x^2 + k_y^2) \hat{P} + \frac{\partial^2 \hat{P}}{\partial z^2}] e^{2\pi i (k_x x + k_y y)} = 0. \tag{B.6}$$

We obtain

$$\frac{\partial^2 \hat{P}}{\partial z^2} - q^2 \hat{P} = 0. \tag{B.7}$$

where

$$q^2 = 4\pi^2 (k_x^2 + k_y^2). \tag{B.8}$$

From Eqn. (B.7), we know that the Fourier coefficients of the pressure are harmonic functions, so they can be expanded as

$$\hat{P} = A(k_x, k_y) \cosh qz + B(k_x, k_y) \sinh qz, \tag{B.9}$$

where $A$ and $B$ are constants to be determined, which depend only on the wavenumbers, independent of $z$.

Substituting Eqn. (B.3a) and Eqn. (B.3b) into the Stokes equation Eqn. (B.1) gives:

$$q^2 \begin{bmatrix} \hat{u} \\ \hat{v} \\ \hat{w} \end{bmatrix} - \frac{\partial^2}{\partial z^2} \begin{bmatrix} \hat{u} \\ \hat{v} \\ \hat{w} \end{bmatrix} + \begin{bmatrix} 2\pi i k_x \hat{P} \\ 2\pi i k_y \hat{P} \\ \frac{\partial \hat{P}}{\partial z} \end{bmatrix} = 0. \tag{B.10}$$

The boundary conditions for $u$ are

$$u \big|_{z=0} = u_1, \quad u \big|_{z=L} = u_2. \tag{B.11}$$

Expand the boundary conditions in Fourier series:

$$u_1 = \sum_{k_x} \sum_{k_y} \hat{u}_1(k_x, k_y) e^{2\pi i (k_x x + k_y y)}, \tag{B.12a}$$

$$u_2 = \sum_{k_x} \sum_{k_y} \hat{u}_2(k_x, k_y) e^{2\pi i (k_x x + k_y y)}. \tag{B.12b}$$

The boundary conditions require that:

$$\hat{u} \big|_{z=0} = \hat{u}_1, \quad \hat{u} \big|_{z=L} = \hat{u}_2. \tag{B.13}$$
Solve the nonhomogeneous equations Eqn. (B.10) for \( \dot{u}, \dot{v}, \) and \( \dot{w} \):

\[
\dot{u} = \frac{\cosh \left( \frac{qz - \frac{qL}{2}}{2} \right)}{\cosh \left( \frac{qL}{2} \right)} \left( \frac{\dot{u}_1 + \dot{u}_2}{2} \right) + \frac{\sinh \left( \frac{qz - \frac{qL}{2}}{2} \right)}{\sinh \left( \frac{qL}{2} \right)} \left( \frac{\dot{u}_2 - \dot{u}_1}{2} \right) + \frac{\pi i k_x}{q} (A \cdot C + B \cdot D),
\]

\[
\dot{v} = \frac{\cosh \left( \frac{qz - \frac{qL}{2}}{2} \right)}{\cosh \left( \frac{qL}{2} \right)} \left( \frac{\dot{v}_1 + \dot{v}_2}{2} \right) + \frac{\sinh \left( \frac{qz - \frac{qL}{2}}{2} \right)}{\sinh \left( \frac{qL}{2} \right)} \left( \frac{\dot{v}_2 - \dot{v}_1}{2} \right) + \frac{\pi i k_y}{q} (A \cdot C + B \cdot D),
\]

\[
\dot{w} = \frac{\cosh \left( \frac{qz - \frac{qL}{2}}{2} \right)}{\cosh \left( \frac{qL}{2} \right)} \left( \frac{\dot{w}_1 + \dot{w}_2}{2} \right) + \frac{\sinh \left( \frac{qz - \frac{qL}{2}}{2} \right)}{\sinh \left( \frac{qL}{2} \right)} \left( \frac{\dot{w}_2 - \dot{w}_1}{2} \right) + \frac{1}{2} (A \cdot E + B \cdot F),
\]

where \( C, D, E, F \) are functions of \( q \) and \( z \):

\[
C = \left( z - \frac{L}{2} \right) \sinh \left( \frac{qz - \frac{qL}{2}}{2} \right) - \frac{L}{2} \cosh \left( \frac{qz - \frac{qL}{2}}{2} \right) \tanh \left( \frac{qL}{2} \right),
\]

\[
D = \left( z - \frac{L}{2} \right) \cosh \left( \frac{qz - \frac{qL}{2}}{2} \right) - \frac{L}{2} \sinh \left( \frac{qz - \frac{qL}{2}}{2} \right) \coth \left( \frac{qL}{2} \right),
\]

\[
E = \left( z - \frac{L}{2} \right) \cosh \left( \frac{qz - \frac{qL}{2}}{2} \right) - \frac{L}{2} \sinh \left( \frac{qz - \frac{qL}{2}}{2} \right) \coth \left( \frac{qL}{2} \right),
\]

\[
F = \left( z - \frac{L}{2} \right) \sinh \left( \frac{qz - \frac{qL}{2}}{2} \right) - \frac{L}{2} \cosh \left( \frac{qz - \frac{qL}{2}}{2} \right) \tanh \left( \frac{qL}{2} \right).
\]

Taking the divergence of Eqn. (B.3a), we get the continuity equation for Fourier expansion:

\[
\nabla \cdot \mathbf{u} = \sum_{k_x} \sum_{k_y} \left( 2\pi i k_x \ddot{u} + 2\pi i k_y \ddot{v} + \frac{\partial \ddot{w}}{\partial z} \right) e^{2\pi i (k_x x + k_y y)} = 0.
\]

So

\[
2\pi i k_x \ddot{u} + 2\pi i k_y \ddot{v} + \frac{\partial \ddot{w}}{\partial z} = 0.
\]

Substituting Eqn. (B.14a) - Eqn. (B.14c) into Eqn. (B.17) and solving for
A and B, we can get:

\[
A = 2 \frac{2\pi i [k_x(\hat{u}_1 + \hat{u}_2) + k_y(\hat{v}_1 + \hat{v}_2)] \sinh \left( \frac{qL}{2} \right) + q(\hat{w}_2 - \hat{w}_1) \cosh \left( \frac{qL}{2} \right)}{qL - \sinh(qL)},
\]

\[
B = -2 \frac{2\pi i [k_x(\hat{u}_2 - \hat{u}_1) + k_y(\hat{v}_2 - \hat{v}_1)] \sinh \left( \frac{qL}{2} \right) + q(\hat{w}_1 + \hat{w}_2) \sinh \left( \frac{qL}{2} \right)}{qL + \sinh(qL)}.
\]

(B.18a)

(B.18b)

B.2 Periodic Boundary Condition in z (2 walls are the same)

When the boundary condition \(u_1\) and \(u_2\) are the same, \(u_1 = u_2 = u_w\) the above expressions can be simplified. The Fourier coefficients \(\hat{u}, \hat{v}\) and \(\hat{w}\) are given by

\[
\hat{u} = \frac{\cosh(qz - \frac{qL}{2})}{\cosh \left( \frac{qL}{2} \right)} \hat{u}_w + \pi_1 \frac{k_x}{q}(A \cdot C + B \cdot D),
\]

(B.19a)

\[
\hat{v} = \frac{\cosh(qz - \frac{qL}{2})}{\cosh \left( \frac{qL}{2} \right)} \hat{v}_w + \pi_1 \frac{k_y}{q}(A \cdot C + B \cdot D),
\]

(B.19b)

\[
\hat{w} = \frac{\cosh(qz - \frac{qL}{2})}{\cosh \left( \frac{qL}{2} \right)} \hat{w}_w + \frac{1}{2}(A \cdot E + B \cdot F).
\]

(B.19c)

A and B will be reduced to

\[
A = 8\pi i \frac{(k_x \hat{u}_w + k_y \hat{v}_w) \sinh \left( \frac{qL}{2} \right)}{qL - \sinh(qL)},
\]

(B.20)

\[
B = -4 \frac{q \hat{w}_w \sinh \left( \frac{qL}{2} \right)}{qL + \sinh(qL)}.
\]

(B.21)
APPENDIX C

DERIVATION OF GREEN’S FUNCTION FOR 2D PERIODIC STOKES FLOW

C.1 2D Periodic Stokes Equation

Assume the domain is $L \times L \times L$ box, periodic in the $x$ and $y$ directions. The force is at $\mathbf{r}_0 = (Z, 0, 0)$, the 2D Stokes equation in dimensionless form is

$$\nabla \cdot \mathbf{u} = 0, \quad \nabla^2 \mathbf{u} = \nabla P + \mathbf{F}(\mathbf{r} - \mathbf{r}_0). \quad (C.1)$$

Expand the flow field $\mathbf{u} = \{u, v, w\}^T$ and pressure $P$ in Fourier series, periodic in the $x$ and $y$ directions:

$$u = \sum_{k_x,k_y} \hat{u}(z)e^{i(k_x x + k_y y)}, \quad (C.2a)$$

$$v = \sum_{k_x,k_y} \hat{v}(z)e^{i(k_x x + k_y y)}, \quad (C.2b)$$

$$w = \sum_{k_x,k_y} \hat{w}(z)e^{i(k_x x + k_y y)}, \quad (C.2c)$$

$$P = \sum_{k_x,k_y} \hat{P}(z)e^{i(k_x x + k_y y)}, \quad (C.2d)$$

where

$$k_x = 2\pi \cdot l, \quad k_y = 2\pi \cdot m, \quad l, m = \ldots -2, -1, 0, 1, 2\ldots$$

Defining $k = \sqrt{k_x^2 + k_y^2}$, no-slip boundary conditions give the value for
\( \dot{u}, \dot{v}, \dot{w} \) on each side of the point force as follows:

\[
\begin{align*}
\dot{u}_L &= A_1 \sinh(kz) + \frac{k_x}{k} z [C_L \cosh(kz) + B_L \sinh(kz)], \\
\dot{v}_L &= A_2 \sinh(kz) + \frac{k_y}{k} z [C_L \cosh(kz) + B_L \sinh(kz)], \\
\dot{w}_L &= A_3 \sinh(kz) + z [B_L \cosh(kz) + C_L \sinh(kz)], \\
\dot{P}_L &= 2 [B_L \cosh(kz) + C_L \sinh(kz)],
\end{align*}
\]

where \( B_L = -kA_3 \) and \( C_L = -i(k_x A_1 + k_y A_2) \).

On the other side, we have

\[
\begin{align*}
\dot{u}_R &= A_4 \sinh(kz') + \frac{k_x}{k} z' [C_R \cosh(kz') + B_R \sinh(kz')], \\
\dot{v}_R &= A_5 \sinh(kz') + \frac{k_y}{k} z' [C_R \cosh(kz') + B_R \sinh(kz')], \\
\dot{w}_R &= A_6 \sinh(kz') + z' [B_R \cosh(kz') + C_R \sinh(kz')], \\
\dot{P}_R &= 2 [B_R \cosh(kz') + C_R \sinh(kz')],
\end{align*}
\]

where \( z' = L - z, B_R = -kA_6 \) and \( C_R = -i(k_x A_4 + k_y A_5) \).

All the coefficients \( A_i \) are determined by the jump conditions at \( z = Z \).

### C.2 \( z \) force

The equations for Fourier coefficients are

\[
\begin{align*}
\frac{i k_x \dot{P}}{\dot{u}_{zz}} - (k_x^2 + k_y^2) \dot{u}, \\
\frac{i k_y \dot{P}}{\dot{v}_{zz}} - (k_x^2 + k_y^2) \dot{v}, \\
\dot{P}_z - \dot{w}_{zz} - (k_x^2 + k_y^2) \dot{w} + \delta(z - Z), \\
0 &= i k_x \dot{u} + i k_y \dot{v} + \dot{w}_z.
\end{align*}
\]

The jump condition is \([\dot{P}] = 1\), while \( \dot{u}, \dot{v}, \dot{w}, \dot{u}_z, \dot{v}_z, \dot{w}_z \) are continuous across the jump.

All these conditions give 8 dependent equations for the 6 \( A_i \) unknowns.
The solutions are

\[ A_1 = -ik_x \frac{z \sinh(kL) \sinh(kL - kx) - kL(L - z) \sinh(kz)}{k[1 + 2k^2L^2 - \cosh(2kL)]}, \]  

\[ A_2 = -ik_y \frac{z \sinh(kL) \sinh(kL - kx) - kL(L - z) \sinh(kz)}{k[1 + 2k^2L^2 - \cosh(2kL)]}, \]  

\[ A_3 = \frac{[1 + 2k^2L(L - z)] \cosh(kz) - \cosh(2kL - kx)}{2k[1 + 2k^2L^2 - \cosh(2kL)]} \]
\[ + \frac{(2L - z) \sinh(kz) - z \sinh(2kL - kx)}{2[1 + 2k^2L^2 - \cosh(2kL)]}, \]  

\[ A_4 = ik_x \frac{(L - z) \sinh(kL) \sinh(kz) - kLz \sinh(kL - kx)}{k[1 + 2k^2L^2 - \cosh(2kL)]}, \]  

\[ A_5 = ik_y \frac{(L - z) \sinh(kL) \sinh(kz) - kLz \sinh(kL - kx)}{k[1 + 2k^2L^2 - \cosh(2kL)]}, \]  

\[ A_6 = \frac{(1 + 2k^2Lz) \cosh(kL - kx) - \cosh(kL + kx)}{2k[1 + 2k^2L^2 - \cosh(2kL)]} \]
\[ + \frac{(L + z) \sinh(kL - kx) - (L - z) \sinh(kL + kx)}{2[1 + 2k^2L^2 - \cosh(2kL)]}. \]  

C.3 \( x \) force

The equations for Fourier coefficients are

\[ ik_x \dot{P} = \dot{u}_{zz} - (k_x^2 + k_y^2)\dot{u} + \delta(z - Z), \]  

\[ ik_y \dot{P} = \dot{v}_{zz} - (k_x^2 + k_y^2)\dot{v}, \]  

\[ \dot{P}_z = \dot{w}_{zz} - (k_x^2 + k_y^2)\dot{w}, \]  

\[ 0 = ik_x \dot{u} + ik_y \dot{v} + \dot{w}_z. \]  

From Eqn. (C.7d) we have

\[ \dot{w}_{zz} = -i(k_x \dot{u}_z + k_y \dot{v}_z), \]  

\[ \ddot{w}_{zzz} = -i(k_x \ddot{u}_{zz} + k_y \ddot{v}_{zz}). \]  

Also, from Eqn. (C.7c) we have

\[ \ddot{P}_z = \ddot{w}_{zzz} - (k_x^2 + k_y^2)\ddot{w}_z. \]
Taking (C.7a) \(-k_x + (C.7b) \cdot k_y\) gives

\[i(k_x^2 + k_y^2) \dot{P} = (k_x \dot{u}_{zz} + k_y \dot{v}_{zz}) - (k_x^2 + k_y^2)(k_x \dot{u} + k_y \dot{v}) + k_x \delta(z - Z). \quad (C.11)\]

Plug in Eqn. (C.9) and Eqn. (C.10) we get

\[i(k_x^2 + k_y^2) \dot{P} = i \dot{w}_{zz} - (k_x^2 + k_y^2)(k_x \dot{u} + k_y \dot{v}) + k_x \delta(z - Z) = i \dot{P}_{zz} + i(k_x^2 + k_y^2)[\dot{w}_{zz} + i(k_x \dot{u} + k_y \dot{v})] + k_x \delta(z - Z). \quad (C.12)\]

So

\[\dot{P}_{zz} - (k_x^2 + k_y^2) \dot{P} - ik_x \delta(z - Z) = 0. \quad (C.13)\]

The jump conditions are \([\dot{P}_z] = ik_x\) and \([\dot{u}_z] = -1\), while \(\dot{u}, \dot{v}, \dot{w}, \dot{P}, \dot{v}_z, \dot{w}_z\) are continuous across the jump.
The solutions are

\[ A_1 = \frac{1}{2k^3 \sinh(kL)[1 + 2k^2 L^2 - \cosh(2kL)]} \{ -2k_y^2 \sinh^2(kL) \sinh(kL - kz) \\
+ kk_x \sinh(kL)[z \sinh(2kL - kz) - (2L - z) \sinh(kz)] \\
+ k^2[2(k_y^2 L^2 - k_z^2 L) \cosh(kz) \sinh(kL) \\
- 4k_y^2 L^2 \cosh(kL) \sinh(kz) - 2 \sinh^2(kL) \sinh(kL - kz)] \\
+ 2k^4 L^2 \cosh(kL) \sinh(kL) \} \], (C.14a)

\[ A_2 = \frac{k_x k_y}{2k^3 \sinh(kL)[1 + 2k^2 L^2 - \cosh(2kL)]} \{ 2 \sinh^2(kL) \sinh(kL - kz) \\
+ k \sinh(kL)[z \sinh(2kL - kz) - (2L - z) \sinh(kz)] \\
- 2k^2 L[(L + z) \cosh(kz) \sinh(kL) - 2L \cosh(kL) \sinh(kz)] \}, (C.14b)

\[ A_3 = -ik_x \frac{kL(L - z) \sinh(kz) + z \sinh(kL) \sinh(kL - kz)}{k[1 + 2k^2 L^2 - \cosh(2kL)]}, (C.14c) \]

\[ A_4 = \frac{1}{2k^3 \sinh(kL)[1 + 2k^2 L^2 - \cosh(2kL)]} \{ -2k_y^2 \sinh^2(kL) \sinh(kz) \\
+ kk_x \sinh(kL)[(L - z) \sinh(kL + kz) - (L + z) \sinh(kL - kz)] \\
+ k^2[2(k_y^2 L^2 - k_z^2 L)(L - z)] \cosh(kL - kz) \sinh(kL) \\
- 4k_y^2 L^2 \cosh(kL) \sinh(kL - kz) - 2 \sinh^2(kL) \sinh(kz)] \\
+ 2k^4 L^2 \cosh(kL) \sinh(kL - kz) \sinh(kL) \}, (C.14d) \]

\[ A_5 = \frac{k_x k_y}{2k^3 \sinh(kL)[1 + 2k^2 L^2 - \cosh(2kL)]} \{ 2 \sinh^2(kL) \sinh(kz) \\
+ k \sinh(kL)[(L - z) \sinh(kL + kz) - (L + z) \sinh(kL - kz)] \\
- 2k^2 L[(2L - z) \cosh(kL - kz) \sinh(kL) - 2L \cosh(kL) \sinh(kL - kz)] \}, (C.14e) \]

\[ A_6 = ik_x \frac{kLz \sinh(kL - kz) + (L - z) \sinh(kL) \sinh(kz)}{2k[1 + 2k^2 L^2 - \cosh(2kL)]}. (C.14f) \]
APPENDIX D

NONDIMENSIONALIZATION FOR MULTI SPECIES EQUATIONS

D.1 Dimensionless Variables

Let $z_0$ and $D_0$ be the reference valence and diffusivity, $c_0$ being the reference concentration, we also has the reference Debye Layer length:

$$\lambda_{D_0} = \sqrt{\frac{\varepsilon_0 K T}{2 z_0^2 e^2 c_0}}. \quad (D.1)$$

For dimensionless time, length and potential, $\tau$, $x$, and $\phi$, we have:

- $\tau = \frac{D_0}{\lambda_{D_0} L} t$: time
- $x = LX$: length
- $\phi = \frac{z_0 e K}{T} \Phi$: potential

For the concentration of the various species, $c'_i$ denotes the dimensional concentration, the dimensionless concentration $c_i$ can be defined by

$$c_i = \frac{c'_i}{2c_0}. \quad (D.2)$$

Here four dimensionless parameters will be used:

- $\frac{\lambda_{D_0}}{L}$
- $\bar{V}$: potential
- $\frac{D_i}{D_0}$: ratio of diffusivity
- $\frac{z_i}{z_0}$: ratio of valences
D.2 Scaling of the One-Dimensional PNP Equations

The PNP equations for species \( i \) are

\[
\frac{\partial c_i}{\partial t} = -\frac{\partial}{\partial X} \left( -D_i c_i \frac{\partial \phi}{\partial X} + \frac{z_i e}{K T} \frac{\partial c_i}{\partial X} \right) = -D_i \frac{\partial}{\partial X} \left( -\frac{z_i e}{K T} c_i \frac{\partial \phi}{\partial X} \right). \tag{D.3}
\]

Nondimensionalizing:

\[
\frac{D_0}{\lambda_{D_0} L} \frac{\partial c_i}{\partial \tau} = D_i \frac{1}{L} \frac{\partial}{\partial x} \left( \frac{1}{L} \frac{\partial c_i}{\partial x} \pm \frac{z_i e}{K T} \frac{c_i}{z_0 e} \frac{1}{L} \frac{\partial \phi}{\partial x} \right). \tag{D.4}
\]

So

\[
\frac{D_0}{\lambda_{D_0}} \frac{\partial c_i}{\partial \tau} = \frac{D_i}{L} \frac{\partial}{\partial x} \left( \frac{\partial c_i}{\partial x} \pm \frac{z_i e}{z_0 c_i} \frac{\partial \phi}{\partial x} \right). \tag{D.5}
\]

Divide by \( 2c_0 \):

\[
\frac{\partial c_i}{\partial \tau} = \frac{D_i \lambda_{D_0}}{D_0} \frac{\partial}{\partial x} \left( \frac{\partial c_i}{\partial x} \pm \frac{z_i e}{z_0 c_i} \frac{\partial \phi}{\partial x} \right). \tag{D.6}
\]

For the Poisson’s Equation, the diffusivity does not appear:

\[
-\nabla \cdot (\varepsilon \nabla \phi) = \rho = \sum_i z_i e c_i, \tag{D.8}
\]

\[
-\frac{\varepsilon}{L^2} \frac{K T}{z_0 e} \nabla^2 \phi = \sum_i z_i e c_i, \tag{D.9}
\]

\[
-\frac{\varepsilon K T}{2 z_0^2 e^2 c_0 L^2} \nabla^2 \phi = \frac{1}{2 z_0 c_0} \sum_i z_i c_i. \tag{D.10}
\]

So in dimensionless form, we have

\[
-\left( \frac{\lambda_{D_0}}{L} \right)^2 \nabla^2 \phi = \frac{1}{2 z_0 c_0} \sum_i z_i c_i. \tag{D.11}
\]

The dimensionless charge density can be set to be:

\[
\rho = \sum_i \frac{z_i e}{z_0} c_i = \sum_i \frac{z_i}{z_0} c_i. \tag{D.12}
\]
D.3 Scaling of Langevin Equation

The Langevin equation is written:

$$dX_i = \mp D_i \frac{z_i e}{K T} \nabla \phi dt + \sqrt{2 \frac{D_i}{K T}} dt \mathbf{n}.$$  \hspace{1cm} (D.13)

Nondimensionalizing:

$$L dx_i = \mp D_i \frac{z_i e}{K T} \frac{K T}{z_0 e L} \nabla \phi \frac{\lambda_{D_0} L}{D_0} d\tau + \sqrt{2 \frac{D_i}{K T}} \frac{\lambda_{D_0} L}{D_0} d\tau \mathbf{n}.$$  \hspace{1cm} (D.14)

So in dimensionless form, it becomes:

$$dx_i = \mp \frac{D_i}{D_0} \frac{z_i \lambda_{D_0}}{z_0 L} \nabla \phi d\tau + \sqrt{2 \frac{D_i \lambda_{D_0}}{D_0 L}} d\tau \mathbf{n}.$$  \hspace{1cm} (D.15)
REFERENCES


