Induced-charge Electrokinetics at Large Voltages

by

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Abstract

The classical transport theory cannot explain the experimental behavior of electrochemical systems in the extreme operating conditions required by modern microfluidics devices. Some experimental puzzles include strange behavior of colloidal particles, high-frequency flow reversal in microfluidic ACEO pumps, and concentration dependence of electrokinetic slip. Theoretical developments would help not only in exploiting poorly understood effects favorably, but also in building more efficient microfluidics devices. The goal of this thesis is to explore possible mechanisms and modifications of the current theory that would enable us to interpret the experimental data. The following is a brief summary of the contributions of this thesis to the subject:

Colloidal Particles. A new invention in colloid science is the Janus particle, which is a two-faced spherical particle where one face is polarizable, and the other non-polarizable. These particles have potential applications in drug delivery, building of nanowires and solar energy.

Experiments show that Janus particles strongly interact with boundaries: they approach walls, swim along walls, or sometimes jump away from walls. We show, by conducting numerical simulations of this truly 3D problem, that at least some of those observations can be explained within the classical linear theory.

Finite Size Effects in Electrolytes. The classical Poisson-Boltzmann (PB) theory of electrolytes assumes a dilute solution of point charges with mean-field electrostatic forces. Even for very dilute solutions, however, it predicts absurdly large ion concentrations (exceeding close packing) for surface potentials of only a few tenths of a volt, which are often exceeded, e.g., in microfluidic pumps and electrochemical sensors.

Since the 1950s, there have been numerous attempts in the literature to incorporate steric effects into the standard models. Most of those theories are complex, and require non-trivial numerical methods even for a simple problem. For this reason, they have not found applications in other contexts such as electrokinetics. In contrast, we focus on qualitative finite size effects, and incorporate only the essential elements of ion-crowding, using a lattice-gas model based statistical mechanical approach. Nonetheless, we are able to reach many conclusions about how steric effects play a role in electrochemical systems at large applied voltages.

While dilute solution theory predicts that the differential double layer capacitance is exponentially increasing, steric effects predict that it varies non-monotonically: the differential capacitance always decays to zero after an initial increase. In addition, the net salt adsorption by the double layers in response to the applied voltage is greatly reduced, and so is the tangential "surface conduction" in the diffuse layer, to the point that it can often be neglected, compared to bulk conduction. This explains why, contrary to PB theory, limiting current is

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rarely attained in experiments.

It has been shown that an asymmetric array of electrodes can be used to pump fluids in micro devices. These pumps operate only with AC voltage. Experiments have demonstrated that, when the AC frequency is high enough, the fluid flow supplied by such pumps reverses. This reversal, while not predicted by any of the standard theories, can be explained using our steric theory.

We also generalize our steric models to the time-dependent case, deriving the first modified Poisson-Nernst-Planck (MPNP) equations, which incorporate finite size effects into the PNP equations. The modified equations should be used instead of PNP when the thin double layer approximation fails and the ion concentrations are high enough to make steric effects important.

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I was also lucky to have Armand Ajdari as a visiting professor at MIT in the academic year 2005-06. I, Martin and him had many fruitful discussions from which a lot of ideas in this thesis came to existence. Armand was the first to suggest studying of the "modified PNP" equations, as well as the composite diffuse layer model among many other things. Having him in the department that year literally more than doubled our productivity, and made possible the completion of the work in chapters 4 and 5. Armand continued to give us feedback to us even after he became the director of R&D in Saint-Gobain. Needless to say, I am deeply indebted to Armand.

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Chapter 1

Introduction

Electrochemical transport is an interesting branch of science because it deals with both physical and chemical processes simultaneously, and it relates to our everyday life in a direct manner. Energy storage and conversion devices, such as batteries and fuel cells, can best be understood in the context of electrochemical transport. Other examples include desalination (by electrodialysis), electroplating, colloid science and microfluidics.

Electrochemical systems are complicated by many factors. Ions interact with each other and the solvent, as well as the electrodes and other boundaries in the system. Ions may acquire solvation shells, adsorpt to surfaces, and surface reactions may take place. In addition, external electric fields are applied to electrolytes in many applications. The goal of electrochemical transport theory is to describe such phenomena.

1.1 Electrokinetics

Electrokinetics is the study of electrically driven fluid flow or particle motion. Nearly two centuries ago, Reuss first observed [149] migration of dispersed clay particles in water under the influence of an electric field, which is known as electrophoresis today. Some fifty years later, Quinke [143] described electro-osmosis with glass capillaries, which would serve as a great experimental setup later for unveiling the secrets of electrokinetic processes. In a seminal paper [80], Helmholtz developed mathematical models, the first of their kind, for electroosmosis and electrophoresis and gave the first derivation of the 'Helmholtz-Smoluchowski slip' formula, which is still in use today. Smoluchowski used this formula so systematically and consistently [172, 173, 174] that he lent his own name to it. He proved [172] in 1905 that the mobility of a colloidal particle with uniform surface charge density is independent of its geometry. All these happened before there was a good understanding of the double layers, whose nonlinear structure were first studied by Gouy [73] and Chapman [40]. In order to cutoff the divergences in the Gouy-Chapman model, Stern proposed [180] the existence of a compact layer at the surface. These earlier works formed the basic tenets of electrokinetics, and have been used to analyze and explain many complex phenomena such as diffusioosmosis [141], surface conduction [48, 53, 51], limiting current [175], and induced-charge electro-osmosis [12, 177].

In earlier days, reasons to study electrokinetics ranged from understanding biological mechanisms, such as water transport in the leaves of a tree, to better characterizing and manipulating
colloidal particles, which play a central role in most ancient and modern craft industries. For example, the cellulose fiber and clay used in paper-making are colloidal, as are many ceramic products made up of clay/water sols. Today, the study of electrokinetic phenomena has become even more important with the advent of microelectromechanical systems (MEMS) technology and advances in biology. Now we can build micron sized devices with integrated micropumps, mixers and detectors to analyze or manipulate colloidal particles, or cells in the blood. Lab work that takes weeks might be possibly done in minutes using a lab-on-a-chip device, or at least, such is the goal of today’s researchers [150].

We are now ready to give a short review on the basic concepts in electrokinetics, such as the electrical double layer, electroosmotic slip and induced-charge electrokinetics. In the next chapter, we are going to give a more mathematical introduction to the basic electrochemical transport theory and electrokinetics as they relate to this thesis work.

Electrical Double Layer

A surface in contact with an electrolyte is usually charged: the surface may be intrinsically charged, it may be a metal electrode charged by an external source, or it may adsorb ions and/or solvent molecules from the electrolyte and therefore possess a net charge. This charged surface then attracts screening counterions from the electrolyte, which form the diffuse layer around the charged surface. This diffuse layer, together with the charged surface layer is called the electrical double layer. The resulting potential difference between the surface and the bulk electrolyte is called the double layer potential, or zeta potential.

In case of polarizable surfaces, such as metal electrodes, the amount of charge in the double layer changes dynamically depending on the external factors. This charging and relaxation process can be modeled by approximating the double layer by a capacitor. However, the double layer capacitance is not constant but a function of the double layer potential or charge density.

Electrokinetic Motion

When an electric field acts on the double layer, ions in the diffuse layer start to move, causing electrokinetic slip. If the double layer belongs to a fixed object, the resulting fluid flow is referred to as electro-osmosis. If the charged surface belongs to a particle, or colloid, the electrokinetic slip causes the particle to swim in the electrolyte. This is called electrophoresis.

The electrokinetic slip is given by the Helmholtz-Smoluchowski (HS) slip formula,

\[ \mathbf{u}_s = -b \mathbf{E}_t = -\frac{\varepsilon_b \Psi_D}{\eta_b} \mathbf{E}_t \]

where \( \mathbf{E}_t \) is the tangential field, \( b = \frac{\varepsilon_b \Psi_D}{\eta_b} \) is the electro-osmotic mobility, \( \Psi_D \) is the diffuse layer potential, and \( \varepsilon_b \) and \( \eta_b \) are the permittivity and viscosity of the bulk solvent.

Electrokinetics in Applications

Electrokinetic phenomena are already being exploited in microfluidic and nanofluidic systems for applications in biology, medicine, analytical chemistry and energy conversion. Electro-osmotic pumps utilize electrokinetic slip to generate fluid motion in microfluidic devices. Those
pumps can be useful for various purposes, like drug delivery [123] or removing excess water from fuel cells [33]. Another example is DNA electrophoresis [110, 147], where DNA fragments are placed in a gel and driven by an electric field. Since smaller molecules tend to move faster, this separates molecular fragments by size.

Theoretical modeling and simulation are crucial in the design and optimization of those microfluidic systems. More importantly, a solid theory that can predict basic experimental observations is needed as a basis for more advanced computer simulations. Unfortunately, we do not still have a unique theory that can explain all the rich observed electrokinetic phenomena. We point out the deficiencies of the classical theory in the coming sections. Improving the current theory is the main goal of this thesis work.

1.2 Induced-Charge Electrokinetics

Scientists used to have a simple understanding of electrokinetics: created flow was proportional to the surface charge times the electric field applied. This is indeed the case when the applied electric field is weak. However, a little thought shows that, a strong electric field will change the distribution of the surface charges and the resulting flows are going to be more complicated. This is why we need a thorough mathematical description to understand electrokinetic phenomena. Even if the surfaces are initially uncharged, the applied electric field causes polarizable surfaces to charge, creating an "induced-charge". Electric field then acts on this induced charge, resulting in electrokinetic flow, called induced-charge electro-osmosis (ICEO) or induced-charge electrophoresis (ICEP).

Therefore the electric field, and its interaction with polarizable surfaces need to be described accurately to calculate electrokinetic flows in a system. Classical electrostatics and conservation laws have been used in the mean-field continuum context to model electrokinetic systems. This has been really fruitful. The standard theory of electrokinetics has played an important role in unraveling the rich nonlinear electrokinetic phenomena. Murtskovkin and his collaborators [64, 126] theorized that polarizable particles would create quadrupolar flow around themselves which has a scaling $u \propto E^2$. Later, they confirmed their ideas experimentally with mercury drops and metal particles [127, 63]. The scaling $u \propto E^2$ is particularly important, because such flows persist in AC fields, where the linear effects averages to zero. In many applications such as microfluidic pumps, use of AC fields is desirable because strong DC fields lead to harmful electrode reactions and bubble formation.

Using the same theory, Ajdari [1] suggested that broken symmetries in a periodic array of electrodes would lead to net flow in one direction and this mechanism could possibly be used to pump fluids. His predictions were later experimentally demonstrated [32, 183] by using planar electrodes of unequal widths and gaps. Bazant and Ben [9] suggested an improved 3D design for such ACEO pumps and predicted an order of magnitude faster flows in simulations. Later, this new design was experimentally verified to bring superior efficiency [189, 190]. On the electrophoretic front, Squires and Bazant [178] studied the theory of partially coated spherical particles (also called Janus particles), predicting their motion under AC fields, which were later confirmed by experiments [66]. Also in this thesis, we use the classical theory to explain why janus particles approach insulating walls in those experiments.

In spite of its great inspirational success, the standard theory for the ICEO is far from complete. Most of the above experiments -while conforming to some of the predictions- had
unexplained features in them: The flow was sometimes in the opposite direction in [127, 63], the asymmetric pumps showed flow reversal at large AC frequencies in experiments of [32, 183], and the flow magnitudes seem to decrease at larger concentrations in [107], whereas concentrations never enter any of the theoretical predictions of the flow speed. In one case [108, 107], the predictions of the nonlinear theory were so unacceptable that the linearized theory was used, although the applied voltages were clearly in the nonlinear regime.

It is one of the goals of this thesis to investigate possible improvements of the classical theory, and to capture some of the unexplained experimental observations. Such a theory would not only help design and optimization of electrokinetic devices but also it would lead to discovery of new nonlinear effects that could be exploited for new applications.

1.3 Finite Size Effects

Finite size effects, or *steric* effects, are caused by the fact that ions and the solvent occupy a certain amount of space, and there is an energy associated with ionic particles squeezed into a small space. The dilute solution theory treats ions and the solvent as mathematical points and does not consider any finite size effects. But do those effects matter? Or more precisely, under what conditions, if at all, do finite size effects become important?

Failure of Dilute Solution Approximation

Dilute solution theory fails when large voltage differences are applied. This theory predicts that the concentration of ionic species follow the Boltzmann distribution and are proportional to $c_0 \exp(\pm \psi / \psi_T)$, where $\psi$ is the electrostatic potential, and $\psi_T = kT/e \approx 25mV$ is the thermal voltage. When the dimensionless potential $\psi / \psi_T$ takes on small or moderate numbers, the concentrations are comparable to their bulk values. However, if $\psi$ gets large compared $\psi_T$ in any region, then the electrolyte -according to the dilute solution theory- is no longer dilute in that region, and the dilute solution theory violates its own assumptions.

In ACEO experiments, in order to achieve the desired flow rates, several volts are applied across the electrodes. But this corresponds to electrode potentials around $\psi / \psi_T \approx \pm 100$, which results in unreasonably high predictions for the concentration field. Therefore the dilute solution theory cannot be applied in the new ACEO context, and it is no surprise that its predictions cannot explain many observed features, such as high frequency flow reversal in asymmetric electrode arrays.

Main Consequences of Finite Size Effects

Therefore, it is crucial to develop electrokinetic models that take into account finite size effects. In this thesis, we analyze the steric effects by simple continuum models. The key results are (i) in contrast with the classical theory, the diffuse layer’s differential capacitance is bounded and decreases at large voltage, and (ii) thus the diffuse layer cannot easily engulf enough ions to perturb the bulk concentration or to conduct significant tangential currents.

In the steric model, the diffuse layer structure has two distinct regions at large voltages. Near the wall, the counterion concentration is constant at its maximum, and there are no coions or solvent. This condensed region is appended by a more traditional transition diffuse layer.
This also motivates us to postulate modifications to the Smoluchowski’s formula, and attribute saturation of electro-osmotic mobility to steric effects as well.

The steric theory begins to explain some of the experimental data, such as high-frequency flow reversal and flow saturation at large concentrations. In addition, we predict new electrokinetic phenomena at large voltages, such as electrophoresis of uncharged particles in an asymmetric electrolyte (an electrolyte where positive and negative ions are very different in size).

1.4 Theoretical Framework

1.4.1 Mean-field theory

A many-body system with interactions is usually a difficult problem which does not possess exact solutions. Mean field theories attempt to approximate the solution of such systems by making reasonable assumptions. Given one ion, molecule or body in general, the mean field theory assumes that the interaction of all other bodies on this body can be replaced with an average or effective interaction. Therefore the N-body problem is now replaced with N one-body problems, which is considerably easier.

For example, in an electrolyte each ion is constantly colliding with other ions and the solvent molecules. In order to exactly know how each species evolves we need to take into account all the interactions between ions and the solvent. However, if we consider just one ion or molecule, the interaction of this particle with all the other species can be thought of as a random walk in the electrolyte domain. In reality, this "random" walker might have a complicated probability distribution function which depends on the locations and velocities of all the other surrounding species. However, since there are a large number of ions, we can approximate this probability function by a uniform one. In short, fluctuations are replaced by a mean effect. This is the gist of the mean-field theory. In MFT, many interactions are replaced by one effective interaction. MFT is more accurate when each particle interacts with a large number of other particles.

1.4.2 Continuum Limit

A continuum is an infinitely divisible body with each piece preserving all the properties of the bulk, and the continuum limit is the assumption that the studied material can be treated as a continuum for all purposes. While we know there is no continuum material, the continuum limit calculations are often very accurate and reflective of the original discrete system. In this thesis, we will remain in the continuum world, because it is convenient and we believe that our results are still qualitatively valid on average even when the continuum assumptions are violated.

1.4.3 Dilute and Concentrated Solution Theories

Another simplification in the electrochemical transport theory is the assumption that the electrolyte solution is infinitely dilute. This means that the ions and the solvent molecules are mathematical points. Therefore, there are no constraints because of the physical size of ions or the solvent. In addition, the interaction between different ion species would be negligible.
Two ion species can migrate in the opposite directions, and there would be no friction between them.

Traditional concentrated solution theory, as presented in [133], takes into account the frictional interaction between different species of ions with each other and the solvent. However, it still considers ions as mathematical points, there are no size constraints on the concentrations. In fact, the steady state solutions of the dilute and the concentrated solution theory are identical.

### 1.4.4 Thesis Framework

In this thesis, we will take a mean-field continuum approach, and consider improvements to the dilute solution theory. Our models remain analytically tractable, yet they are an important improvement to the dilute solution theory, in the following: (i) Our models obey the physical size limit for ion concentrations. (ii) Our models explain some of the experimental findings that dilute solution theory fails to predict.

This is not to say that our steric models are accurate in every sense. Our hope is that our models are descriptive on average, and they are useful in the modeling work in many fields such as microfluidics.

### 1.5 Outline of thesis

The outline of this thesis is as follows: In chapter 2, we give a concise summary of main concepts in electrochemical transport and electrokinetics. This covers the basic background, and puts our work in context. In chapter 3, we employ the classical theory of chapter 2 on janus particles, and demonstrate a mechanism for why those particles approach walls, as observed in recent experiments. This also shows the success of the traditional theory in the low-voltage regime. In chapter 4, we examine an analytically tractable theory that incorporates finite size effects into the general theoretical framework of the dilute solution theory. We argue that steric effects result in a condensed layer near the surface, and imply bounded non-monotonic double layer capacitance, which decreases at large voltages. We continue in chapter 5 by extending the steric theory to electrolyte dynamics. We derive the modified Poisson-Nernst-Planck equations, and demonstrate it on the model parallel-plate problem. We shift gears in chapter 6, and investigate implications of finite size effects on electrokinetic phenomena. In this chapter, we suggest modifications for the Smoluchowski’s slip formula and their implications. We also consider ACEO pumps with our steric models, and show that finite size effects may explain the high frequency flow reversal observed in the experiments conducted on ACEO asymmetric arrays. Finally, we conclude in chapter 7 by summarizing our results and suggesting future research directions.

### 1.6 Related Publications

- **Chapter 3**: M.S. Kilic, and M.Z. Bazant, Wall effects in induced charge electrophoresis, submitted to Phys. of Fluids.


Chapter 2

Classical Theory

In this chapter, we give a brief summary of the classical theory of electrochemical transport and electrode reaction processes. We start in section 2.1 with the Poisson-Nernst-Planck (PNP) equations, which describe the concentration dynamics in a dilute electrolyte, and can be found in any standard electrochemistry textbook [133, 23, 89]. In this section, we analyze the steady state solutions to PNP equations, and also mention the concentrated solution theory of [133], and how it relates to our work. We also give a derivation of the chemical potential, sometimes not readily found in the literature, but essential to our coming chapters on finite size effects.

In section 2.2, we introduce the standard double layer theories in conjunction with the PNP equations, and in section 2.3 we connect them together in the thin double layer limit. A mathematical formalization of this approximation will be given later in chapter 5 in the context of modified PNP equations. In the remaining sections, we cover the basic theory of electrokinetics, including the Helmholtz-Smoluchowski formula and its derivation, electrophoretic mobility of colloidal particles, as well as examples of induced-charge electrokinetics. We end the chapter by mentioning some experimental data and puzzles that are not explained well by the standard theory.

2.1 Poisson-Nernst-Planck Equations

In a continuum model, the dynamics of ion concentrations are governed by the conservation law

\[
\frac{\partial c_i}{\partial t} = -\nabla \cdot \mathbf{F}_i
\]  

(2.1)

where \( c_i \) and \( \mathbf{F}_i \) denote the concentration and flux density of species \( i \). There are no source terms on the right hand side of (2.1), indicating our assumption that no chemical reactions that consume or produce any species occur in the bulk.

2.1.1 Ion Transport in Dilute Solutions

For a dilute electrolyte near equilibrium, the velocity of ion \( i \) is proportional to gradient of its chemical potential

\[
\mathbf{v}_i = -b_i \nabla \mu_i
\]

(2.2)

where \( b_i \) is the ions mobility.
Another assumption, and the basis of dilute solution theory is that the chemical potential of a point-like ion $i$ has the simple form,

$$\mu_i = kT \ln c_i + z_i e \psi$$  \hfill (2.3)

where $z_i e$ is the charge, $c_i$ the concentration, and $\psi$ the electrostatic potential. The form (2.3) is sometimes called the “ideal” component of the chemical potential \cite{69}, to which various “excess” components at finite concentration can be added.

Using only the ideal component of the chemical potential, the flux density is

$$F_i = c_i v_i = -b_i c_i \nabla \mu_i$$

$$= -D_i (\nabla c_i + \frac{z_i e}{kT} c_i \nabla \psi)$$ \hfill (2.4)

where Einstein’s relation, $D_i = b_i / kT$, which relates the ion’s mobility $b_i$ to its diffusivity $D_i$, has been used to obtain the last equality. The first term in (2.4) represents the diffusive flux, whereas the second term accounts for the migration due to the electric field.

The Nernst-Planck equation can be obtained by plugging (2.4) into the conservation law:

$$\frac{\partial c_i}{\partial t} = D_i \left[ \nabla^2 c_i + \frac{z_i e}{kT} \nabla \cdot (c_i \nabla \psi) \right]$$ \hfill (2.5)

The equation system is closed by the Poisson’s equation

$$-\nabla \cdot (\varepsilon \nabla \psi) = \rho = \sum_i z_i e c_i.$$ \hfill (2.6)

typically with a constant permittivity $\varepsilon$. Together, (2.5) and (2.6) are called Poisson-Nernst-Planck (PNP) equations.

2.1.2 Concentrated Solution Theory

In a concentrated solution, the equation (2.2) is sometimes replaced by the more general formulation

$$c_i \nabla \mu_i = kT \sum_j \frac{c_i c_j}{c_T D_{ij}} (v_j - v_i)$$ \hfill (2.7)

where $c_T = \sum_i c_i$ is the total concentration, including the solvent, and $D_{ij}$ is a diffusion coefficient describing the interaction of species $i$ and $j$. In words, the driving force $c_i \nabla \mu_i$ on the left hand side of (2.7) is balanced by the frictional forces between species $i$ and all others. This system can be solved to yield flux densities in the form

$$F_i = -c_i \sum_j L_{ij} \nabla \mu_j$$

where $L_{ij}$ are generalized mobilities that reflect frictional interactions between different species.

While this is a more general setting than (2.2), the chemical potential (2.3) needs to be modified for highly concentrated solutions, or even for dilute solutions under large applied voltages. The concentrated solution theory describes the dynamic interactions (i.e. frictions)
between species, yet if used with (2.3), it still fails to capture finite size effects, which prevail even in the presence of a single ion species.

2.1.3 Steady State

Since the driving force of ion transport is the gradients in the chemical potentials, the steady state of the electrolyte corresponds to a system with constant chemical potentials for all species. For dilute solutions, this yields a Boltzmann distribution

\[ c_i = c_i^0 e^{-z_i e \psi / kT} \]  

(2.8)

with a reference concentration \( c_i^0 \).

The steady-state solutions are the same for the dilute and concentrated solution theories. This further illustrates our view that the concentrated solution theory fails to describe finite size effects.

**Poisson-Boltzmann Equation**  
The concentrations (2.8), when used in the Poisson equation (2.6), give the Poisson-Boltzmann (PB) equation

\[-\nabla \cdot (\varepsilon \nabla \psi) = \sum_i z_i e c_i^0 e^{-z_i e \psi / kT}\]

In most situations, the PB equation does not allow for analytical progress, and it is linearized for small potentials \( |\psi| << \psi_T \), to yield the Debye-Huckel equation

\[-\nabla \cdot (\varepsilon \nabla \psi) = \sum_i z_i e c_i^0 (1 - \frac{z_i e}{kT} \psi)\]

At equilibrium, the solution is electroneutral, so the first term in the summation vanishes and we obtain

\[-\nabla \cdot (\varepsilon \nabla \psi) = \sum_i z_i^2 e^2 c_i^0 \psi\]

or, when \( \varepsilon \) is assumed constant,

\[ \nabla^2 \psi = \frac{1}{\lambda_D^2} \psi \]

where

\[ \lambda_D = \sqrt{\frac{\varepsilon kT}{\sum_i z_i^2 e^2 c_0}} \]  

(2.9)

is the Debye length, in which we assume that the permittivity \( \varepsilon \) is constant. The Debye length is typically in the range 1 – 100 nm, and it is the length scale over which an ionic charge or a charged surface is screened. This also shows that the width of the screening diffuse layer near a boundary scales with \( \lambda_D \).

Both the PB equation, and its Debye-Huckel linearization have analytical solutions in 1-D for a symmetric \( z : z \) binary electrolyte. We will review those solutions while discussing diffuse layer models in the next section.
2.1.4 Electroneutrality

A common assumption is that of local electroneutrality in the bulk:

\[ \sum_i z_i c_i = \rho = 0 \]  \hspace{1cm} (2.10)

The physical intuition is clear: The electric forces created by any charge imbalance in the bulk would strongly act so as to make the bulk charge free. Mathematically, the equation (2.10) can be derived from the Poisson’s equation (2.6) by noticing that the left hand side remains "small" in the bulk. After rescalings

\[ x' = x/L, \; c'_i = c_i/c_0, \; \psi' = \psi/\psi_T \]

where \( L \) is the characteristic length, \( c_0 \) the bulk concentration, and \( \psi_T = kT/e \) the characteristic thermal potential, the Poisson equation becomes

\[ \rho' = \sum_i z_i c'_i = \frac{\lambda_p^{\frac{3}{2}}}{L^2} \sum_i \frac{z_i^2}{2} \nabla^2 \psi' \]  \hspace{1cm} (2.11)

As the Debye length is usually much smaller than any other geometric length in the system, the right hand side of (2.11) is nearly zero. This argument shows that bulk solution does not have any regions with significant charge density.

However, near the system boundaries, there may exist highly charged regions, referred to as diffuse layers. The characteristic width of the diffuse layer is the Debye length (2.9) as can be seen from the equation (2.11). It turns out that these thin layers play significant role in electrokinetic phenomena, and they are certainly worth further careful study. We will consider the diffuse layer models in the next section.

2.1.5 Boundary Conditions

In this thesis, we do not focus on electrode reactions, and we will stick with the blocking electrode boundary conditions

\[ \mathbf{n} \cdot \mathbf{F}_i = 0 \]  \hspace{1cm} (2.12)

where \( \mathbf{n} \) denotes the normal to the boundary. This holds at the real boundary of the system, and we will see the asymptotic approximations to the PNP equations where (2.12) is replaced with nonzero flux boundary conditions. In that case, the computational domain -theoretically- does not include the diffuse layers, although this does not change its size or shape in practice.

2.1.6 Derivation of Chemical Potential

In order to derive the chemical potential (2.3) from a statistical mechanics framework, we first calculate the Helmholtz free energy

\[ F = U - TS \]
and use the fact that the chemical potential equals the functional derivative of free energy with respect to concentration

\[ \mu_i = \frac{\delta F}{\delta c_i} \]  

(2.13)

This formula is only natural, because the chemical potential is defined to be the energy needed to add an infinitesimal quantity of a species holding everything else constant.

**Internal Energy** For simplicity, let us consider a binary \( z : z \) electrolyte and assume that zero Neumann boundary conditions \( \mathbf{E} \cdot \mathbf{n} = 0 \) hold at the boundaries. For general case, the arguments below are similar, with some extra boundary terms.

Recall that, in the end, we want to calculate the functional derivative of internal energy \( U \) with respect to variations in concentrations \( \delta c \pm \). Although the electrostatic energy of a system is given by

\[ W = \int \frac{\varepsilon}{2} \mathbf{E}^2 d\mathbf{r}, \]

this form is not appropriate for our purposes, because all the effect coming from the variations \( \delta c \pm \) enter through the electric field \( \mathbf{E} \).

Instead, we will use the equivalent form

\[ U = \int \left( \frac{\varepsilon}{2} \mathbf{E}^2 - \lambda |\nabla \cdot (\varepsilon \mathbf{E})| - z \varepsilon (c_+ - c_-) \right) d\mathbf{r}. \]

where \( \lambda \) is a Lagrangian multiplier. If we choose \( \lambda \) such that

\[ \frac{\delta U}{\delta \mathbf{E}} = \varepsilon \mathbf{E} + \varepsilon \nabla \lambda = 0 \]

(2.14)

then, we can take the variational derivative in \( \delta c \pm \) without worrying about the variational changes \( \delta \mathbf{E} \). The equation (2.14) implies \( \mathbf{E} = -\nabla \lambda \), and hence \( \lambda = \psi \) up to a constant.

Using some vector identities, we find that

\[ U = \int d\mathbf{r} \left( -\frac{\varepsilon}{2} |\nabla \psi|^2 + z \varepsilon c_+ \psi - z \varepsilon c_- \psi \right). \]

(2.15)

Now we can differentiate this expression with respect to concentrations \( c \pm \), without worrying about how \( \delta c \pm \) alters the electric field \( \mathbf{E} = -\nabla \psi \), because of equation (2.14). What about the effect of \( \delta c \pm \) on the potential \( \psi \)? Since \( \psi = \lambda \) was the Lagrangian multiplier, we also have \( \frac{\delta U}{\delta \psi} = 0 \), when Poisson equation holds. So, we do not have to worry about \( \psi \) either. In the end, we will obtain

\[ \frac{\delta U}{\delta c \pm} = \pm z \varepsilon \psi \]

which has been tantalizing, yet very intuitive at the same time.

**Entropic contribution** The entropic contribution is

\[ -TS = \frac{kT}{a^3} \int \left[ c_+ a^3 \ln (c_+ a^3) + c_- a^3 \ln (c_- a^3) \right] d\mathbf{r}, \]

(2.16)
where $c_{\pm}a^3$ is considered to be the probability of an ion species to exist in a particular cell of size $a^3$, which normalizes the integral. We assumed that the effective ion size is $a$, for both species, although this is not necessary to carry on the calculation here. Later, when dealing with steric effects, this assumption will be needed for analytical progress.

Using the formulae (2.15) and (2.16) in (2.13), we derive the chemical potential given in (2.3). Later, we will work with a different free energy and derive the resulting chemical potential in the same way.

### 2.2 Double Layer Models

Traditionally, the electrical double layer consists of two distinct parts: the compact and the diffuse layers. The chemical interaction even between a flat surface and the electrolyte is complicated: solvent molecules, or even ions may adsorb (i.e. stick) to the surface, regardless of their charge, forming a complex structure. Because of their size, and obstruction from the adsorbed solvent molecules or ions, or a dielectric coating, the free floating ions in the solution cannot get closer to the surface than some certain points, which define the outer Helmholtz plane (OHP). The messy region between the surface and the OHP constitutes the compact layer, also known as Stern layer.

Outside the OHP, the ions -even if they are strongly attracted to the charged surface- are, by definition, not static but subject to thermal motion. Diffuse layer is made up by those thermally oscillating ions that screen the charged surface. We now explain the classical models of the diffuse and the compact layers in more detail.

#### 2.2.1 Diffuse Layer Models

Near a charged flat surface, there forms a diffuse layer of thickness $O(\lambda_D)$. If this length scale is much smaller than other geometric features in the system, which it usually is, we can practically ignore the transverse variations in the quantities of interest. Mathematically, this corresponds to the scaling $\tilde{x} = xL/\lambda_D$, while keeping $y$ and $z$ scalings the same in the diffuse layer, which now corresponds to $x > 0$, $x = O(1)$. Therefore all the $y$ and $z$ derivatives vanish, and we are left with 1-D versions of the equations.

To simplify the algebra, we limit ourselves to the symmetric $z : z$ electrolyte, that is $z_i = z_+ = -z_- = z$. This is not too restrictive, because usually the diffuse layer is dominated by only one type of ions -those that have the opposite sign to that of the surface.

**Gouy-Chapman Model**

The one dimensional PB equation for a semi-infinite electrolyte reads

$$
\varepsilon \frac{\partial^2 \psi}{\partial x^2} = 2z e \varepsilon_0 \sinh \left( \frac{z e \psi}{kT} \right), \quad x > 0
$$

(2.17)

with boundary conditions

$$
\psi = \Psi_D \text{ at } x = 0, \quad \psi \rightarrow 0 \text{ at } x \rightarrow \infty
$$

(2.18)
Figure 2-1: Schematic picture of the compact (Stern) and the diffuse layers near a charged surface. The electric potential (b) and average ion concentrations (c) are also shown. Note that the diffuse layer scales with $\lambda_D \approx 1 - 100 \text{nm}$, and is several hundred times thicker than the ion diameter, contrary to what (a) might suggest.

The diffuse layer potential drop $\Psi_D$ is sometimes called the $\zeta$ potential, but we will reserve $\zeta$ for description of electro-osmotic mobility. This equation was first solved by Gouy [73] and then independently by Chapman [40], and the solution is

$$\psi = 4 \frac{kT}{ze} \tanh^{-1}(\tanh(\frac{z\psi_D}{4kT})e^{-x/\lambda_D})$$

(2.19)

which quickly vanishes as the ratio $x/\lambda_D$ gets larger, confirming our predictions about the thickness of the diffuse layer. This thin diffuse layer however possesses a charge density per unit area of

$$q = \int_0^\infty \rho dx = \varepsilon \frac{\partial \psi}{\partial x} |_{x=0}$$

$$= -4ze\varepsilon_0 \lambda_D \sinh\left(\frac{z\psi_D}{2kT}\right)$$

(2.20)
which can get large at high voltage differences. The differential capacitance of the surface is then

\[ C_D = -\frac{dq}{d\Psi_D} = \frac{\varepsilon}{\lambda_D} \cosh \left( \frac{ze\Psi_D}{2kT} \right) \]  

(2.21)

This capacitance blows up exponentially at large voltage drops, which implies very slow charging of the double layer.

**Debye-Huckel Model**

At small voltages \(|\Psi_D| < \psi_T\), the solution (2.19) can be linearized to yield

\[ \psi = \Psi_D e^{\mp \zeta / \lambda_D} \]  

(2.22)

which shows exponential decay in the concentration of screening charges. This exponential profile also corresponds to the solution of the Debye-Huckel equation linearization of (2.17) with the corresponding boundary conditions (2.18). The charge density of the diffuse layer is given by the linear relationship \( q = \frac{\varepsilon}{\lambda_D} \Psi_D \), corresponding to a linear capacitor with permittivity \( \varepsilon \) and plate separation \( \lambda_D \).

### 2.2.2 Compact Layer

The simplest model for the compact layer is when it is assumed charge free. In this case, the potential varies linearly in the compact layer, and we have

\[ V = \Psi_D - \lambda_S \frac{\partial \psi}{\partial x} \]  

(2.23)

where \( V \) is the potential at the surface, and \( \lambda_S \) is the effective compact layer thickness, which, for a simple dielectric layer, is its actual thickness multiplied by the ratio \( \varepsilon / \varepsilon_S \) of the dielectric constants of the solvent and the compact layer. We can rewrite equation (2.23) as

\[ \Psi = \Psi_D + \lambda_S \frac{q}{\varepsilon} \]  

and differentiate with respect to \( q \) to obtain

\[ \frac{1}{C} = -\frac{d\Psi}{dq} = \frac{d\Psi_D}{dq} + \frac{\lambda_S}{\varepsilon} = \frac{1}{C_D} + \frac{1}{C_S} \]  

where \( C_S = \varepsilon / \lambda_S \) is the Stern capacitance. Therefore, the compact layer acts as a capacitor in series with the diffuse layer.

The ratio of the compact and linear diffuse layer capacitances is sometimes denoted by \( \delta = \frac{C_S}{C_D} \). Using this parameter, the differential capacitance in the Gouy-Chapman-Stern model is given by

\[ C = \frac{\varepsilon}{\lambda_D} \frac{1}{\delta + [\cosh(\frac{ze\Psi_D}{2kT})]^{-1}} \]  

(2.24)

which, unlike (2.21), remains bounded. This is one of the reasons why the compact layer model has gained popularity, because the exponentially large values of (2.21) at high voltages...
are usually unphysical and do not conform with experiments. Additionally, since it is hard to directly measure $\delta$, the compact layer formulation provides help with an additional fitting parameter in the interpretation of experimental data.

2.3 Electrochemical Relaxation

So far, we have been interested in the equilibrium structure of the double layers. What about the electrochemical dynamics? A simple but useful approach is to model the double layer and the bulk with an effective capacitance and resistance. This simple RC circuit model is widely recognized in electrochemistry [171, 119, 68] as a first approximation to electrochemical dynamics, and it is also known as the weakly nonlinear approximation.

The basic intuition is that the equilibration time of the double layer is fast compared to the dynamics of the global "circuit" considered, essentially because it is so thin so that transport processes within the double layer are rapid. The circuit model also assumes that the double layer charge intake is not large enough to cause significant perturbations in the bulk concentration. A mathematical justification, starting from the PNP equations, can be given in terms of an asymptotic analysis of the thin double layer limit [13].

Therefore, we anticipate that for the many situations where the double layer is thin compared to the system size, the dynamics can be understood to a significant extent using the equilibrium characteristics of the double layer. These then provide appropriate boundary conditions for the dynamic transport processes in the bulk.

2.3.1 Bulk as a Resistor

In many cases, such as when applied voltages and other perturbations are small, the bulk concentrations do not fluctuate significantly in space and time. By summing up the ion fluxes, we get the current as

$$J = \sum_i z_i F_i = - \sum_i z_i D_i (\nabla c_i + \frac{z_i e}{kT} c_i \nabla \psi) \quad (2.25)$$

When the bulk concentrations $c_i$ are constant, the first term in the summation drops out, and we are left with

$$J = - \sum_i \frac{D_i}{kT} z_i^2 e c_i \nabla \psi = \kappa E \quad (2.26)$$

where $\kappa = \kappa(c_i) = \sum_i \frac{D_i z_i^2 e c_i}{\kappa}$ is the ionic conductivity, here a constant. Physically, this means that the bulk can be treated as an effective resistance when concentration variations are negligible. If not, the bulk still behaves like a resistance except it also generates a diffusion current, given by the first term in (2.25). However, all of these conclusions are invalid when concentrations are time-dependent.

2.3.2 The RC Circuit

In one dimension, the double layers and the bulk together constitute a simple RC circuit system, described by

$$\frac{dq}{dt} = -C \frac{d\psi}{dt} = -J \cdot n \quad (2.27)$$
where \( q \) is the double layer charge, fed by the normal bulk current density \(-\mathbf{J} \cdot \mathbf{n}\) (the normal \(-\mathbf{n}\) points toward the surface). The characteristic charging time at small voltages for this capacitor is given by

\[
\tau_c = RC = C \frac{L}{\kappa} = \frac{\lambda_D L}{D}
\]

which is much smaller than the bulk diffusion time \( \tau_d = L^2 / D \) in the case of thin double layers \( \lambda_D << L \). This confirms the basic intuition of the electric circuit model.

### 2.3.3 Weakly Nonlinear Model

The RC Circuit described above is more generally known as the weakly nonlinear model, and it can be used for any geometry in one or more dimensions. The two main premises of the weakly nonlinear regime, in mathematical terms, are: (i) The double layers are thin and they are always in equilibrium, and (ii) Outside the double layers, the concentrations stay constant, so \( c_i = c_0 \).

In the weakly nonlinear model, we only solve for the bulk potential using the Laplace’s equation

\[
\nabla^2 \psi = 0
\]

which comes from (2.26) and conservation of charge \( \nabla \cdot \mathbf{J} = 0 \) in a potential field with \( \mathbf{E} = -\nabla \psi \). The double layers are modeled by the surface charge \( q \), and the double layer potential drop \( \zeta = \psi_s - \psi \), where \( \psi_s \) is either imposed by an external source (e.g. electrodes), or it is determined from a charge conservation relation (e.g. for colloidal particles). For polarizable surfaces, the constitutive relation \( q = q(\zeta) \) is given by the linear, Gouy-Chapman or an MPB model of the double layer, whereas \( q = \zeta = 0 \) holds for insulating surfaces. The boundary condition (2.27) is therefore enough to close the system.

According to [13], and also our analysis in chapter 5, the weakly nonlinear model is valid until the salt uptake by the double layers gets high enough to perturb the bulk concentrations significantly. During the charging time, scaled as \( \tau_c = \frac{\lambda_D L}{D} \), diffusing ions can cover only a distance \( l_D = \sqrt{\tau_c D} = \sqrt{\lambda_D L} \), which is the length scale of the diffusion layer. If the excess salt uptake by the double layers

\[
w = \lambda_D \int_0^\infty (c^\text{inner}_+ + c^\text{inner}_- - 2c_0) dx_{\text{inner}}
\]

is comparable to the ionic content of diffusion layer, \( c_0 l_D = c_0 \sqrt{\lambda_D L} \), then the weakly nonlinear regime breaks down. The salt uptake \( w \) is a surface quantity just like the double layer charge \( q \), and is a function of \( \zeta \) (and \( c_0 \), if not constant). In the Gouy-Chapman model, \( w = 8c_0 \lambda_D \sinh^2 \left( \frac{\zeta c_0 \kappa}{4kT} \right) [13] \), which leads to exponentially large values of \( w \) at high voltages, and therefore the weakly nonlinear model breaks down quickly in the dilute solution theory. However, the dilute solution theory also breaks down at those large voltages. We will see in chapter 5 that steric theories predict milder dependence of the salt uptake \( w \) on \( \zeta \), and hence justify the usage of the weakly nonlinear model for a larger set of situations.
2.3.4 Strongly Nonlinear Effects

Many interesting phenomena are predicted beyond the weakly nonlinear regime. At very high voltages, the double layer can take in so much salt that the bulk gets completely depleted of ions, which is called the space-charge phenomenon[43]. In this regime, the electrolyte structure near the surface expands and behaves in a more complicated way, certainly not described well by a simple circuit. Another important nonlinear effect not described by the weakly nonlinear theory is the surface conduction[44]. This refers to the transverse migration and diffusion of the ions in the double layer, that may become significant at large voltages.

The strongly nonlinear problem is formulated in [42], and is beyond the scope of this thesis. As mentioned in the previous subsection, finite size effects make it harder -but not impossible- for electrolyte systems to experience strongly nonlinear effects. The implications of the steric theories presented herein in the strongly nonlinear regime are left for future work.

2.4 Electro-osmotic Slip

In general, the fluid motion in the electrolyte is governed by the Navier-Stokes equations

\[ \rho_m \left[ \frac{\partial \mathbf{u}}{\partial t} + (\mathbf{u} \cdot \nabla) \mathbf{u} \right] = -\nabla p + \nabla \cdot (\eta \nabla \mathbf{u}) + \rho \mathbf{E} \]

\[ \nabla \cdot \mathbf{u} = 0 \]

where \( \mathbf{u} \) is the fluid velocity (all species are assumed to have the same velocity), \( p \) the pressure, \( \rho_m \) the mass density, \( \eta \) dynamic viscosity which may depend on concentrations \( c_i \) and the electric field \( \mathbf{E} \), and lastly \( \rho \mathbf{E} \) is the electrical body force on the fluid due to charge density \( \rho \), and the electric field \( \mathbf{E} \). More generally, the viscosity \( \eta \) may have a directional dependence as well.

In most cases of interest, such as most biological fluids, the inertial terms (i.e. terms on the left hand side) can be neglected, and we are left with the Stokes equations

\[ \nabla p = \nabla \cdot (\eta \nabla \mathbf{u}) - \rho \mathbf{E} \quad (2.28) \]

along with incompressibility \( \nabla \cdot \mathbf{u} = 0 \).

Due to electroneutrality, the charge density \( \rho \) -and hence the electrical body force- is small in the bulk away from the boundaries. However, when a tangential electric field acts on a charged double layer on a boundary, it does induce fluid motion there, observed as electrokinetic slip on the surface from a macroscopic viewpoint. We now calculate this slip velocity by peeking into the double layer structure.

2.4.1 Electrokinetic Slip Formulae

Let us consider a charged flat surface at \( x = 0 \), with the electrolyte standing in the semi-infinite region \( x > 0, -\infty < y < \infty \) (in 2-D). On this surface, there exists a tangential electric field \( E_y = -\frac{\partial \varphi_b}{\partial y} \). To probe into the double layer structure, we rescale \( x \) by \( \tilde{x} = xL/\lambda_D = x/\epsilon \), with \( \epsilon = \lambda_D/L \ll 1 \), while keeping \( y \) the same.
Electro-osmosis

At leading order, the $y$-component of equation (2.28) is

$$\frac{\partial p}{\partial y} = \frac{\partial}{\partial \hat{x}} \left( \eta \frac{\partial u_y}{\partial \hat{x}} \right) - E_y \frac{\partial}{\partial \hat{x}} \left( \varepsilon \frac{\partial \psi}{\partial \hat{x}} \right)$$

(2.29)

When charging is uniform along the surface, pressure gradients along the surface are negligible, i.e. $\partial p/\partial y = 0$ (see diffusio-osmosis below), then we can integrate the remaining equation to obtain

$$\eta \frac{\partial u_y}{\partial \hat{x}} = E_y \varepsilon \frac{\partial \psi}{\partial \hat{x}}$$

plus a constant. That constant is zero (or $O(\varepsilon)$ to be precise), because in the bulk, both sides are $O(\varepsilon)$, as $u_y$ and $\psi$ scale with $L$. Integrating one more time, we obtain

$$u_y = -E_y \int_0^{\Phi} \frac{\varepsilon(y, \Phi)}{\eta(y, \Phi)} d\Phi$$

(2.30)

where we used the fact that $\Phi \equiv \psi - \psi_b = \Psi$ at the "no-slip" surface $u_y = 0$, with $\psi_b$ being the bulk potential just outside the double layer. If the bulk is in equilibrium, $\psi_b = 0$. The dependence of $\varepsilon$ and $\eta$ on $y$ comes through the bulk concentration $c_b$ and potential $\psi_b$. The equation (2.30) is known as the generalized Helmholtz-Smoluchowski (HS) formula.

There are two slight holes in the above argument: (i) the assumption of $\partial p/\partial y = 0$ (ii) the implicit assumption that the electric field $E_y$ persists inside the diffuse layer. This is not true.
when the surface is ideally polarizable, for example, in the case of AC electroosmotic pumps, because there is clearly no tangential electric field on a metal surface. We now present a careful analysis below.

**Diffusio-osmosis**

Let us analyze the equations (2.28) without assuming that the pressure is constant along the surface. The first equation in (2.28), at leading order, reads

$$\frac{\partial p}{\partial \hat{x}} = \rho(y, \Phi) \frac{\partial \psi}{\partial \hat{x}}$$  \hspace{1cm} (2.31)

where we have assumed that the charge density \( \rho = \rho(y, \Phi) \) is a function of the location \( y \) along the surface and potential difference \( \Phi = \psi - \psi_b \) from the bulk. This is true for equilibrium theories of the double layer, such as Gouy-Chapman-Stern model, which asserts

$$\rho = 2c_b(y) \sinh \Phi$$

Integration of (2.31) yields the electro-osmotic pressure inside the diffuse layer as

$$p = p_b + \int_0^\psi \rho d\Phi \equiv p_b + Q(y, \Phi)$$  \hspace{1cm} (2.32)

Plugging this into the second equation (2.29), and using \( \partial Q / \partial \Phi = \rho \), we obtain

$$\frac{\partial p_b}{\partial y} + \frac{\partial Q}{\partial y} + \rho \frac{\partial \Phi}{\partial y} = \frac{\partial}{\partial \hat{x}} \left( \eta \frac{\partial u}{\partial \hat{x}} \right) + \frac{\partial}{\partial \hat{x}} \left( \varepsilon \frac{\partial \psi}{\partial \hat{x}} \right) \frac{\partial \psi_b}{\partial y}$$

Note that, for the electrical body force in the diffuse layer we use \( -\rho \frac{\partial \psi}{\partial y} \), not necessarily a constant. Fortunately, this term magically cancels with \( \rho \frac{\partial \psi}{\partial y} \) to yield \( \rho \frac{\partial \psi_b}{\partial y} \). Assuming there are no pressure gradients in the bulk, and rearranging we obtain

$$\frac{\partial Q}{\partial y} = \frac{\partial}{\partial \hat{x}} \left( \eta \frac{\partial u}{\partial \hat{x}} \right) + \frac{\partial}{\partial \hat{x}} \left( \varepsilon \frac{\partial \psi}{\partial \hat{x}} \right) \frac{\partial \psi_b}{\partial y}$$

Integrating this equation twice, we obtain

$$u_{y} = k_E \frac{\partial \psi_b}{\partial y} - k_c \frac{\partial c_b}{\partial y}$$  \hspace{1cm} (2.33)

with coefficients

$$k_E = \int_0^\psi \frac{\varepsilon(y, \Phi)}{\eta(y, \Phi)} d\Phi = \frac{\varepsilon_b}{\eta_b} \zeta_{ek}$$

$$k_c = \int_0^\psi \left( \int_0^\psi \frac{\partial Q}{\partial y} \left( \frac{\partial \Phi}{\partial \hat{x}} \right)^{-1} d\Phi \right) \left( \frac{\partial \Phi}{\partial \hat{x}} \right)^{-1} d\Phi$$

Here \( \zeta_{ek} = \zeta_{ek}(\Psi) \) is the effective surface potential, \( \varepsilon_b \) and \( \eta_b \) are respectively bulk permittivity and viscosity. We can think of the quantity \( \zeta_{ek} \) as a surface slip coefficient in units of voltage.
that measures the surface charge density.

The first term in (2.33) is the electro-osmotic slip formula, where we emphasize that the electric field is measured outside the diffuse layer. The second term represents diffusio-osmotic slip, due to concentration gradients along the surface. Those concentration gradients may be induced by the excessive salt intake by the double layers at high voltage regime. We will see that finite size effects reduce the salt intake, and hence diffusio-osmotic phenomena may not be as strong as it is predicted by dilute solution theory.

2.5 Electrophoresis

Electrophoresis is the motion of charged particles suspended in an electrolyte under the influence of an electric field. Electrophoretic motion is not mainly caused by electrostatic forces on the particle [89]. In fact, a particle considered together with its screening diffuse layers is neutral. Rather, electrophoretic motion results from electrokinetic slip induced by the electric field acting on the diffuse layers surrounding the particle. In other words, the particle swims through the electrolyte by creating flow currents around it.

Let us consider a spherical particle, with uniform fixed surface charge density $+q$, which attracts a screening diffuse layer with charge density $-q$. This charge density corresponds to a uniform zeta potential $-\zeta_{ek}$. When an electric field $E$ is turned on, there will be electrokinetic fluid slip on the particle surface in the direction of $E_{//}$, i.e. the tangential component of the electric field on the particle surface. It is tempting to conclude that this slip would drag the particle with itself, but this is not correct way of thinking. The slip velocity is with respect to the particle, in other words the particle is pushing the fluid to create the slip on its boundaries. Therefore the particle moves in the opposite direction as the slip velocity, that is in $(+E)$ direction, as it would if there was no electrolyte.

The electrolyte does make a difference however. Consider two spherical particles of different radii $R_i$, with same fixed uniform surface density on them. In the absence of screening
electrolyte, the electrostatic force on the particle would scale with the total charge of particles, which scales as $R^2$, whereas the Stokes drag would increase only linearly in the radius. Therefore the larger sphere would move faster by the same electric field.

### 2.5.1 Classical electrophoresis

When there is a screening electrolyte, and the slip velocities on the two particles are the same, resulting in the same electrophoretic velocity for both particles. The electrophoretic velocity is also independent of particle shape as well. This remarkable result (due to [125]) can be seen by noting that for any colloidal particle $P$ (with uniform $\zeta_{ek}$ on its surface) the hydrodynamic problem

$$\nabla^2 \mathbf{u} = \nabla p, \quad \nabla \cdot \mathbf{u} = 0,$$

$$\mathbf{u}_{\partial P} - U_P = \mathbf{u}_{\text{slip}} = -\frac{\varepsilon \zeta_{ek}}{\eta} \mathbf{E}_{\parallel} \text{ on } \partial P, \quad \mathbf{u} \to \mathbf{0} \text{ as } |\mathbf{x}| \to \infty$$

is solved by

$$\mathbf{u} = -\frac{\varepsilon \zeta_{ek}}{\eta} (\mathbf{E} - \mathbf{E}_\infty), \quad U_P = \frac{\varepsilon \zeta_{ek}}{\eta} \mathbf{E}_\infty, \quad p = 0$$

where $\mathbf{E}$ solves the electrostatic problem

$$\nabla \cdot \mathbf{E} = 0, \quad \nabla \times \mathbf{E} = 0,$$

$$\mathbf{n} \cdot \mathbf{E} = 0 \text{ on } \partial P, \quad \mathbf{E} \sim \mathbf{E}_\infty \text{ as } |\mathbf{x}| \to \infty$$

Therefore the particle mobility

$$b = \frac{U_P}{E} = \frac{\varepsilon \zeta_{ek}}{\eta}$$

is determined only by $\zeta_{ek}$, independently from particle size or shape.

This is bad news for those who want to use electrophoresis as a means of separating particles, and has diverted their attention towards other methods, like use of gels for DNA separation. In addition, the electrophoretic velocity depends linearly on the electric field strength $E$, and therefore there is no motion under AC fields.

Fortunately, the classical theory of electrophoresis does not apply in most situations, since most particles are polarizable to some extent and their surface charge density is influenced by the applied electric fields. These polarization effects lead to rich phenomena that could be exploited in electrokinetic applications.

In fact, experiments refute the classical theory. Murtsovkin and his coworkers studied irregular quartz particles in a uniform AC field, and observed that they move in directions apparently set by their shape. This conflicts with the classical theory on two different aspects: (i) theory predicts no net motion under an AC field (ii) mobility should not depend on particle shape.

### Mobility of Charged Polarizable Particles

As the electric field gets larger, the particle gets more and more polarized, which affects its mobility in a nonlinear fashion. For an ideally polarizable sphere of radius $R$, the first correction
to mobility is given by

\[ b \sim \frac{\varepsilon_b}{\eta_b} \left[ \zeta_{ek} - \frac{3}{8} \left( \frac{d}{d\psi} \log C \right) \psi = \zeta_{ek} (ER)^2 + \ldots \right] \]  

(2.34)

where \( C \) is the differential capacitance of the thin double layers surrounding the particle. This differential capacitance may be equal to (2.24), or it may be coming from some other model of the double layer (such as the ones we consider in chapter 4).

This is an important result because it predicts that spherical particles can be electrophoretically separated by size using an unbalanced AC field such that \( \langle E \rangle = 0 \), but \( \langle E^3 \rangle \neq 0 \). Such an AC field would cancel the linear part of the electrophoretic velocity, while amplifying the nonlinear corrections whose magnitude depends strongly on the particle size. Although the above analysis concerns only spherical particles, it is not hard to conclude that similar effects hold for particles of general shape.

The formula (2.34) also provides a criterion for when the particle is in the fixed surface charge regime: as long as the second term in (2.34) remains much less than the first term.

2.5.2 Induced-charge Electrophoresis

For neutral particles, the linear contribution to electrophoretic mobility is zero and there are only polarization effects. If the particle is asymmetric, those effects create a quadrupolar flow around it, but there is no net motion. For asymmetric particles, however, polarization effects result in shape-dependent mobility. Bazant and Squires [178] studied nonlinear electrophoresis of polarizable particles with broken symmetry, concluding that such particles can move and rotate in essentially arbitrary directions. This explains the seemingly random behaviour of irregular quartz particles, observed earlier by Murtsovkin and his co-workers [127, 64].

Another example of broken symmetry are the janus particles, which are metallic spherical particles that are half coated with insulating material. In an electric field, such particles rotate to align the interface between the metallic and insulating sides with the field axis. At the same time, the electrokinetic flow on the metallic side of the particle propels it in the direction of the insulating side, with a velocity

\[ U = \frac{9 \varepsilon R E^2}{64 \eta (1 + \delta)} \]

in the linear limit (that is, assuming constant differential capacitance equal to \( 1/(1 + \delta) \)). Therefore, the particle always eventually moves perpendicular to the electric field, with its azimuthal angle set by its initial orientation.

In experiments, janus particles are observed to be attracted by nearby glass walls, where predicted transverse motion takes place. In chapter 3, we argue that this attraction may be caused by the tilting of the janus particle towards the wall as a result of ICEP torque. However, we are not sure what balances this torque near the wall at low AC frequencies, as alone it would rotate the particle completely towards the wall. In that case, the particle would stop moving transversely along the wall, which has not been observed experimentally.
2.5.3 Electrophoresis at Large Voltages

When the voltage drop $ER$ is significant, the correction terms take over the linear one in (2.34), and we are in the nonlinear regime. We will show that, with capacitance taken from the dilute solution theory as in (2.24), the mobility quickly vanishes at large $ER$. This is because the dilute solution theory predicts logarithmic dependence of zeta potential on charge density, which gets flat at large surface charge densities. The exponential decay of the mobility is not observed in experiments, which highlights another shortcoming of the dilute solution theory. We will show that steric theories predict more reasonable dependence of mobility at large applied fields.

2.6 Induced Charge Electroosmotic Flow

Until now, we have been focusing on induced charge effects on particle mobility and electrophoresis, and not so much on fluid motion. With the advent of microfluidics, there has been great interest in electrokinetic phenomena which can be exploited to build pumps and mixers to drive fluid flows. Having no moving parts, those devices are more attractive than their mechanical counterparts for reasons of reliability and durability.

2.6.1 Induced Charge Electro-osmosis

Induced-charge electroosmosis (ICEO) refers to flow generation near a polarizable surface by the action of an electric field on its own diffuse charge. A simple example is an uncharged spherical particle, which does not move but create a quadrupolar flow around itself in response to an electric field. Also, there is no "pumping" in any particular direction. In order to create pumping motion, we need to break the symmetry, such as in the example of a fixed Janus particle, whose metal hemisphere would act like a fixed jet engine driving fluid flow.

In general, any field applied on a polarizable surface at an oblique angle generates ICEO slip. The perpendicular component of the field creates an induced charge, on which the tangential component acts to generate fluid motion. If the field strength is doubled, so are both its components, increasing the slip fourfold. If the sign of this field is switched, both of the components point backwards, yet the electrokinetic slip stays the same. This crucial property, the $E^2$ scaling of ICEO flow, enables us to use AC sources as a driving force in microfluidics.

2.6.2 AC Electro-osmosis

AC fields are more suitable for using in microfluidic devices, because they minimize damaging electrochemical reactions at the electrodes. Besides, it is hard to create steady electric fields by using electrodes in an electrolyte as they are promptly screened by counterions, killing the applied electric field quickly. In contrast, AC fields do not have this difficulty except at low frequencies.

Using fixed polarizable posts in the channel might be one way to build electro-osmotic pumps, but those geometries are far from optimal both in terms of manufacturing and efficiency, especially when half of the electric field is already screened at the electrodes before it hits the slip generating structure. Instead, it is more efficient to generate slip right at the electrodes, in which case the screening charges work in our favor. To this end, electrodes should be placed so
that the generated electric field is oblique to them. One example is two electrodes sitting side by side on an insulating flat surface.

Fluid flow is generated by application of an AC field on these two electrodes as follows (refer to Fig.2-4): Imagine the electrode on the right has potential $V_0 \cos(\omega t)$, whereas the one on the left has $-V_0 \cos(\omega t)$, and consider the times $t = 2\pi k$ for some integer $k$. The electrode on the right (left) has been charging for a while and it has acquired a negatively (positively) charged diffuse layer. There is an electric field from the left electrode towards the right electrode, whose perpendicular component continues to charge the electrodes. The tangential component of this electric field causes slip to the left (right) on the left (right) electrode. At times $t = \pi + 2\pi k$, the signs of the electric field and the diffuse layer charges both switch, creating the same slip pattern on the electrodes. Averaged over time, fluid rolls are created inside the electrolyte.

Because the proposed structure in the last paragraph is symmetric, no pumping motion occurs. However, Ajdari [1] pointed out that directional flow can be generated if the symmetry is broken by coating either of the electrodes by dielectric material. In that case, the slip on the coated electrode would be reduced, and the fluid flow is dominated by the slip on bare electrode, creating a net flow in its direction. Brown, Smith and Rennie [32] implemented this idea, but by breaking the symmetry with uneven electrode widths and gaps. They were able to achieve velocities over 100 microns/sec in the expected direction, confirming the theory, although some unexpected flows in the reverse direction also showed up at high forcing frequencies.

Bazant and Ben [9] recently suggested a novel non-planar electrode design which dramatically enhances the pumping efficiency by an order of magnitude for the same voltages and the minimum feature size. They observed that for the symmetric array of electrodes, most of the slip is generated on a short section of the electrode near the smaller gap. The idea is to raise the sections of the electrodes that supply the slip in the desired direction, so that the slip in the opposing direction now creates circular flow rolls that even help the pumping, in which they call a "fluid conveyor belt" flow structure (see figure 6-7). There is also no flow reversal at high frequencies, however there may exist double peaks in the pumping velocity as a function of forcing frequency (which remains unexplained to date). Generating fluid velocities

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Figure 2-4: Electro-osmotic flow created by two electrodes sitting next to each other on an insulating surface. (a) Electrode and screening diffuse layer charges, and electric field lines (b) Resulting electrokinetic slip and flow.
in the mm/sec range, this 3D design may enable the use of ACEO pumping in portable or implantable microfluidic devices.

Another way to drive a directional ACEO flow is by the use of traveling wave voltages over a periodic array of electrodes[34, 144]. The goal is to eliminate electrokinetic slip in the opposing direction altogether by using a separate set of electrodes for charging and generation of electric field. In the usual design, there is a phase lag of 90 degrees between two adjacent electrodes, so the array is periodic with the length of four electrodes and gaps. An electrode achieves its maximum positive (or negative) charge density just before its potential hits zero (closer to zero at higher frequencies). At this time, its adjacent electrodes have potentials ±V₀ (or ±V₀), supplying the electric field to create the electrokinetic slip on the highly charged electrode in the same direction in both cases. This argument may not hold at lower frequencies, but simulations show that flow should still be created in the same direction. TWEO pumps have been built and tested recently by Garcia-Sanchez et al.[67] While the pumps generate the expected flow at low voltages, they surprisingly show strong flow in the opposite direction at high voltages, especially at low AC frequencies. Researchers are still trying to understand the mechanisms that lead to this unexpected behaviour of the TWEO pumps.

2.6.3 Discrepancy with Experimental Data

Most of the time, the classical theory does slightly better than for the case of TWEO pumps: it at least predicts the flow direction correctly. However, in all the experiments until now, the standard models always overpredicted the magnitude of the flow by a correction factor, Λ⁻¹, which has a wide range from unity to several hundreds in experiments [77, 76, 31, 190, 176, 14, 108, 66], listed in the table 2.1. The correction factor is usually justified by the existence of a thick compact Stern layer [23], which accounts for a large portion of the double layer voltage drop (Λ/(1+Λ) volts for each volt). At low applied voltages, the theory sometimes capture qualitative features of the data and the Stern layer allows for a match on more quantitative terms. However, with increasing applied voltages and bulk concentration, the standard model with the compact layer breaks down and ceases to explain the experiments even qualitatively[67, 183].

For example, the model cannot account for the the adverse effect of increasing ionic concentrations on the flow strength, which is consistently observed for electroosmotic flows and pumps. Recent experimental work [183, 14, 107] suggests that there is a universal logarithmic decay of the pumping velocity \( U \propto \log(\text{c}_{\text{crit}}/\text{c}_0) \). This same trend is also confirmed by the decay of electrophoretic mobility of the Janus particles[66]. The critical concentration, when the flow completely vanishes, is about \( c_{\text{crit}} = 10mM \), unfortunately much below the concentration of typical biological solutions. This phenomenon is yet to be explained, as existing theories predict neither such strong concentration dependence nor a critical concentration at which the flow vanishes. It is also not understood why and how the ion type affects the electrokinetic flow.

As the above examples show, there are many unexplained phenomena in the world of ACEO. We think that this is because the current theories lack a thorough understanding of the electrokinetic slip processes in the double layer structure at large voltages, as also noted in the papers [32, 77]. It is one of the main goals of this thesis (addressed mostly in chapter 6, and appendices) to address this issue. In this thesis, we propose a mechanism for flow reversal in the planar pumps, and attribute it to crowding of the ions. The double peaks in the 3D pumps may
<table>
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<th>$\Lambda$</th>
<th>$\zeta_{\max}$</th>
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<td>0.1mM</td>
<td>0.57V</td>
<td>0.076</td>
<td>0.043</td>
<td>1.7</td>
</tr>
<tr>
<td>[32]</td>
<td></td>
<td>NaNO 3</td>
<td>0.1mM</td>
<td>0.28V</td>
<td>0.081</td>
<td>0.023</td>
<td>0.92</td>
</tr>
</tbody>
</table>

Table 2.1: A table of (inverse) correction factors for various experiments from the literature. When not provided, we estimated $\Lambda$ using our computations. The * indicates that empirical double layer impedance models are used. The † indicates that we roughly accounted for the wall interactions using our models in chapter 3. Also listed are $\zeta_{\max} = \Lambda V_{induced}^{\max}$, and $e\zeta_{\max}/kT \approx 40\zeta_{\max}$, which roughly indicate the maximum effective zeta potential on the diffuse layers.
also originate from asymmetric crowding of ions with a similar mechanism, although we were not able to confirm this in our simulations. The concentration dependence may be explained by increased viscosity in the diffuse layer along with steric effects, but then this theory ceases to explain the flow reversal. So far, we have not been able to combine these two effects together to explain the flow reversal and the concentration dependence simultaneously. There is a lot of research to be done in this field, and our work is only a first attempt at building a much needed successful theory for ACEO and electrochemical dynamics in general.
Chapter 3

Wall interactions in ICEP

Induced-charge electrophoresis (ICEP) has mostly been analyzed for asymmetric particles in an infinite fluid, but channel walls in real systems further break symmetry and lead to dielectrophoresis (DEP) in local field gradients. Zhao and Bau [199] recently predicted that a metal (ideally polarizable) cylinder is repelled from an insulating wall in a DC field. We revisit this problem with an AC field and show that attraction to the wall sets in at high frequency and leads to an equilibrium distance, where DEP balances ICEP, although, in three dimensions, a metal sphere is repelled from the wall at all frequencies. This conclusion, however, does not apply to asymmetric particles. Consistent with the recent experiments of Gangwal et al.[66], we show that a metal/insulator Janus particle is always attracted to the wall in an AC field. The Janus particle tends to move toward its insulating end, perpendicular to the field, but ICEP torque rotates this end toward the wall. Under some conditions, the theory predicts steady translation along the wall with an equilibrium tilt angle, as seen in experiments, although more detailed modeling of the contact region of overlapping double layers is required.

3.1 Introduction

Most theoretical work on electrophoresis has focused on spherical particles moving in an infinite fluid in response to a uniform applied electric field [4, 115, 89, 161]. Of course, experiments always involve finite geometries, and in some cases walls play a crucial role in electrophoresis. The linear electrophoretic motion of symmetric (spherical or cylindrical) particles near insulating or dielectric walls [125, 94, 95, 96, 97, 57] and in bounded cavities or channels [200, 104, 105, 167, 41, 109, 86, 46, 87, 85] has been analyzed extensively. Depending on the geometry and the double-layer thickness, walls can either reduce or enhance the translational velocity, and the rotational velocity can be opposite to the rolling typical of sedimentation near a wall. The classical analysis for thin double layers assumes “force-free” motion driven by electro-osmotic slip alone, but recent work has shown that electrostatic forces can also be important near walls [196, 88]. Heterogeneous particles with non-uniform shape and/or zeta potential exhibit more complicated bulk motion [3, 58, 110, 111], which can also affect boundary interactions [185], especially if the particles are deformable, as in the case of chain-like biological molecules [147].

In this chapter, we focus on the effect of nonlinear induced-charge electro-osmotic (ICEO)
flows at polarizable surfaces, which are finding many new applications in microfluidics and colloids [12, 177, 179]. The canonical example of quadrupolar ICEO flow around a polarizable particle, first described by Murtsovkin [126, 64], involves fluid drawn in along the field axis and expelled radially in the equatorial plane in an AC or DC field. Broken symmetries in this problem can generally lead to hydrodynamic forces and motion induced-charge electrophoresis (ICEP), as well as electrical forces and motion by dielectrophoresis (DEP). Such phenomena have only been analyzed for isolated asymmetric particles in an infinite fluid [12, 195, 178] or in a dilute solution far from the walls [162, 153]. In contrast, experiments demonstrating translational ICEP motion have involved strong interactions with walls [127, 65], which remain to be explained.

As shown in Figure 3-1, it is easy to see that the quadrupolar ICEO flow around a polarizable particle typically causes attraction to unscreened conducting walls (perpendicular to the field) and repulsion from insulating walls (parallel to the field). The former effect of ICEP attraction to conducting walls has not yet been analyzed; it may play a role in colloidal self assembly on electrodes applying AC voltages [188, 197, 168, 151, 152]. This phenomenon is mainly understood in terms of electrohydrodynamic flows (what we would term “ICEO”) induced on the electrodes, not the particles (typically latex spheres), but ICEP could be important for more polarizable particles.

The latter effect of ICEP repulsion from insulating walls has recently been analyzed by Zhao and Bau [199] in the case of a two-dimensional ideally polarizable cylinder in a DC field. However, this phenomenon has not yet been confirmed experimentally. On the contrary, Gangwal et al. [66] have recently observed that metallo-dielectric Janus particles are attracted

Figure 3-1: Hydrodynamic forces on polarizable particles near (a) insulating and (b) unscreened conducting walls due to ICEO flows
to a glass wall, while undergoing ICEP motion parallel to the wall and perpendicular to an applied AC field. It is not clear that the existing theory of ICEP can explain this surprising behavior.

The objective of this work is to analyze the motion of three-dimensional polarizable particles near insulating walls in AC fields. As summarized in section 3.2, we employ the standard low-voltage model in the thin double-layer approximation, following many authors [8, 177, 108, 195, 178], including Zhao and Bau [199]. In section 3.3, we first analyze ideally polarizable cylinders and spheres near a non-polarizable wall, which only experience forces perpendicular to the wall. In section 3.4 we then study spherical metal/insulator Janus particles, which are half ideally polarizable and half non-polarizable. Due to their broken symmetry, the Janus particles also experience ICEP and DEP torques, which strongly affect their dynamics near the wall.

3.2 Mathematical Model

3.2.1 Low Voltage Theory

In this chapter, we will consider either a cylindrical or a spherical particle of radius $a$ in a semi-infinite electrolyte bounded by a plane. The closest distance between the particle and the plane is denoted by $h$. In the absence an applied electric field, we assume that the particle and the wall surfaces are uncharged. In addition, we will assume the electrolyte has a low Reynolds number, and impose Stokes equations. We will assume that the thin double layer approximation holds and the bulk electrolyte remains electroneutral, which is the case when the Debye length

$$\lambda_D = \sqrt{\frac{\varepsilon kT}{2z^2 e^2 c_0}}$$

is much smaller than the characteristic length scale (in our case, $a$). The Debye length typically ranges between $1 - 100 nm$, and colloidal particles are usually in the $\mu m$ range, therefore the thin double layer approximation holds for most of the time.

Then the general equations consist of the Laplace’s

$$\varepsilon \nabla^2 \phi = 0$$

and Stokes equations

$$\eta \nabla^2 \mathbf{u} = \nabla p$$
$$\nabla \cdot \mathbf{u} = 0$$ (3.1)

where $\phi$ is the electrostatic potential and $\varepsilon$ the permittivity, $\eta$ the viscosity of the electrolyte, $\mathbf{u}$ the velocity field and $p$ the pressure. The wall boundary $z = 0$ is an insulator, satisfying

$$\mathbf{n} \cdot \nabla \phi = 0$$

whereas the particle surface, being polarizable, acts as a capacitor in the thin double layer limit

$$\frac{dq}{dt} = (\mathbf{n}) \cdot (-\kappa \nabla \phi)$$
with $q$ being the surface charge density on the particle, $\kappa$ the conductivity of the bulk electrolyte. Far away from the particle, an electric field

$$\nabla \phi \sim E_\infty = E_\infty \hat{x}, \ |x| \to \infty$$

is applied. In general, the magnitude $E_\infty = E_\infty(t)$ may be time dependent.

The Stokes equations are supplied by the no-slip conditions on the wall and the Smoluchowski's electrokinetic slip formula on the particle

$$u = u_{\text{slip}} = \frac{\varepsilon}{\eta} \zeta \nabla_s \phi$$

where $\zeta$ is the potential difference between the surface and the bulk. Lastly, we assume flow vanishes at the infinities.

So far, the equations are complete except for a constitutive relation between $\zeta$ and $q$. The linear theory asserts that

$$q = -\frac{\varepsilon}{\lambda_D} \zeta$$

although the complete problem is still nonlinear in this case because of the quadratic slip formula (3.5). In this chapter, we will study only the linear theory, but the calculations can be repeated with (sometimes more accurate) nonlinear theories like that of Poisson-Boltzmann.

### 3.2.2 Force and Torque on the Particle

Throughout this chapter, we will assume that the particle is fixed and calculate the forces on the particle. For the case of a moving particle, the slip velocity needs to be modified to account for the motion of the particle surface.

The total force and torque on any volume of the fluid are conveniently given in terms of the stress tensor, $\sigma$, by

$$F = \int_{\partial \Omega} n \cdot \sigma dA \quad (3.2)$$

$$T = \int_{\partial \Omega} r \times (n \cdot \sigma) dA \quad (3.3)$$

The stress tensor contains contributions from electrical and viscous stresses on the fluid, $\sigma = \sigma_M + \sigma_H$, where

$$\sigma_M = \varepsilon[EE - \frac{1}{2} E^2 I]$$

$$\sigma_H = -pI + \eta (\nabla u + (\nabla u)^T)$$

are the Maxwell and hydrodynamic stress tensors, respectively.

### 3.2.3 Particle Dynamics

In order to calculate the movement of a colloidal particle, we need to find a translational velocity $U$, and a rotational velocity $\Omega$ such that the net force on the particle is zero, when the slip
velocity is modified by taking into account the velocities $U$ and $\Omega$. In other words, we are seeking $U$ and $\Omega$ such that the problem (3.1) with boundary condition

$$u = u_{slip} + U + r \times \Omega$$

yields $F = 0$ and $T = 0$.

Since the Stokes problem is linear, there is a linear relationship between the translational and rotational motion of the particle and the resulting force and torque exerted on it by the fluid. Let us denote this relationship by

$$\begin{pmatrix} F \\ T \end{pmatrix} = M \begin{pmatrix} U \\ \Omega \end{pmatrix}$$

The viscous hydrodynamic tensor $M$ comes from solving for the Stokes flow around a particle moving with translational velocity $U$ and rotational velocity $\Omega$, assuming no slip on all particle and wall surfaces.

If we then solve the electrokinetic problem for a fixed particle in the applied field, we obtain the ICEO slip velocity $u_{slip}$ as well as the total (hydrodynamic + electrostatic) force $F_{slip}$ and torque $T_{slip}$ needed to hold the particle in place, thereby preventing ICEP and DEP motion.

Using these calculations and invoking linearity, the condition of zero total force and torque on the particle, $\begin{pmatrix} F \\ T \end{pmatrix} + \begin{pmatrix} F_{slip} \\ T_{slip} \end{pmatrix} = 0$, determines the motion of the particle

$$\begin{pmatrix} U \\ \Omega \end{pmatrix} = -M^{-1} \begin{pmatrix} F_{slip} \\ T_{slip} \end{pmatrix} \quad (3.4)$$

The particle trajectory is then described by the solution to the differential equation

$$\frac{dx}{dt} = U$$

together with the equations for the particle's angular orientation.

This angular orientation does not matter for a fully polarizable or insulating particle. For the Janus particle, we will argue that only rotations about $x-$axis are important, thus we will focus on the dynamics of just a single angle. In this case, the equation of motion is simply

$$\frac{d\theta}{dt} = \Omega_x$$
3.2.4 Nondimensional Equations

We nondimensionalize the variables by

\[ x' = \frac{x}{a}, \quad \phi' = \frac{\phi}{E_\infty a}, \quad \zeta' = \frac{\zeta}{E_\infty a} \]
\[ q' = \frac{\varepsilon E_\infty a}{\lambda_D} q \]
\[ t' = \left( \frac{\lambda_D a}{D} \right)^{-1} t = \frac{t}{\tau_c}, \quad t'' = \left( \frac{\eta}{\varepsilon E_\infty^2} \right)^{-1} t = \frac{t}{\tau_u} \]
\[ u' = u \left( \frac{\varepsilon E_\infty^2 a}{\eta} \right)^{-1}, \quad p' = \frac{p}{\varepsilon E_\infty^2} \]

Note that there are two time scales in the problem, \( \tau_c = \frac{\lambda_D a}{D} \), the charging time, and \( \tau_u = \frac{\eta}{\varepsilon E_\infty^2} \), the time scale for particle motion (unit displacement time).

Plugging in the equations, we obtain (after dropping the primes except for \( t \))

\[ \nabla^2 \phi = 0 \]
\[ \nabla^2 u = \nabla p \]
\[ \nabla \cdot u = 0 \]

with the boundary conditions

\[ \frac{dq}{dt'} = n \cdot \nabla \phi \]
\[ u = \zeta \nabla_s \phi \]

(3.5)
on the particle surface, where \( \zeta = \phi_{\text{surface}} - \phi_{\text{bulk}} \) is the zeta potential. For a polarizable particle, we have \( \phi_{\text{surface}} = 0 \) by symmetry, therefore we are left with \( \zeta = -\phi_{\text{bulk}} = -\phi \).

In addition, we have

\[ \nabla \phi \sim \hat{x}, |x| \to \infty \]

just as before, now with the dimensionless variables. The remaining equations are the no-slip boundary condition on the planar wall, and the requirement that the flow vanishes at infinities.

The constitutive relation between \( q \) and \( \zeta \) takes the simple form

\[ q = -\zeta = \phi \]

for the linear theory that we are going to analyze in this chapter.

The dimensionless force and torque on the particle are given by the formulae (3.2) and (3.3), where the stress tensors are replaced by their dimensionless counterparts

\[ \sigma_M = \mathbf{E} \mathbf{E} - \frac{1}{2} E^2 \mathbf{I} \]
\[ \sigma_H = -p \mathbf{I} + (\nabla u + (\nabla u)^T) \]
The force, angular momentum and stress tensors are scaled to

\[ F_{\text{ref}} = \varepsilon E_0^2 a, \quad T_{\text{ref}} = \varepsilon E_0^2 a^2, \quad \sigma_{\text{ref}} = \varepsilon E_0^2. \]

Finally, the particle motion will be governed by

\[ \frac{dx}{dt''} = U, \quad \frac{d\theta}{dt''} = \Omega_x. \]

### 3.2.5 Simplifications

#### Steady Problems

If a DC voltage is applied, then the system reaches a steady state after a while and the time derivatives drop out. This is the case when Neumann boundary conditions are valid also on the cylinder or sphere. In that case

\[
F_E = \int_{\partial \Omega} (E \cdot E - \frac{1}{2} E^2 I) n dA \\
= \int_{\partial \Omega} (E \cdot E - \frac{1}{2} E^2 n) dA = -\frac{1}{2} \int_{\partial \Omega} E^2 n dA
\]

because \( E \cdot n = 0 \) on the surface. As a consequence, the electrostatic torque induced on the particle is zero.

#### Symmetry

For the full cylinder problem, the electrostatic problem has an odd symmetry in the \( x \)-direction, that is

\[ \phi(x, z) = -\phi(-x, z) \]

and for the full sphere problem, it has an odd symmetry in the \( x \)-direction and an even symmetry in the \( y \)-direction:

\[ \phi(x, y, z) = \phi(x, \pm y, z) = -\phi(-x, y, z) \]

As a result, \( E^2 \) has even symmetry in \( x \) and \( y \). Therefore, in the steady case, the electrostatic forces vanish in those directions, and there can only be a vertical force. In general time-dependent cases, \( E \) has an even symmetry in \( x \) and odd symmetry in \( y \), and therefore the electrostatic force may not vanish in the \( x \)-direction.

As for the Stokes problem, a glance at the slip formula shows that the slip, just like the potential field, has an odd symmetry in both \( x \) and \( y \), and therefore so does the flow field. Consequently, there are no hydrodynamic forces in those directions.

Needless to say, all these symmetry arguments disappear for the Janus particles.
**AC fields**

In the linear model we are considering, the time-periodic electrostatic forcing problem can be solved by letting

\[ \phi = \text{Re}(\tilde{\phi} e^{i\omega t}) \]

and solving for the complex potential \(\tilde{\phi}\) using the equations

\[ \nabla^2 \tilde{\phi} = 0 \]

with the boundary conditions

\[ n \cdot \nabla \tilde{\phi} = i\omega \tilde{\phi} \quad \text{(polarizable)} \]
\[ n \cdot \nabla \tilde{\phi} = 0 \quad \text{(insulator)} \]
\[ \tilde{\phi} = E_\infty x \quad \text{(at infinity)}. \]

In the high frequency limit, the electrostatic problem approaches the solution of the Dirichlet problem, that is, the first boundary condition is replaced by

\[ \tilde{\phi} = 0 \quad \text{(polarizable)} \quad (3.6) \]

This is because \( \tilde{\phi} \approx n \cdot \nabla \tilde{\phi} / i\omega \approx 0 \). Physically, this means that the double layers do not have enough time to charge when the forcing frequency is too high. Note that in cases of AC fields below, it is the field amplitude \( E_\infty \) that enters into the scalings above, and the \( U \) is the time-averaged velocity.

Once the electrostatic potential is calculated, the time-averaged slip velocity can be obtained by the formula

\[ u_s = \frac{1}{2} \text{Re}[\tilde{\zeta} \tilde{E}_{///}^*] \quad (3.7) \]

where \( \tilde{\zeta} \) is the (complex) surface zeta potential, which is equal to \( -\tilde{\phi} \) in the linear theory, and \( \tilde{E}_{///}^* \) is the complex conjugate of the tangential component of \( \tilde{E} = \nabla \tilde{\phi} \), the complex electric field. In the DC limit as \( \omega \to 0 \), the imaginary parts of the solutions go to zero, and we are left with \( u_s = \frac{1}{2} \tilde{\zeta} E_{///} \), which is the standard Smoluchowski’s formula with a factor of 1/2.

**3.2.6 Numerical Methods**

We have solved the equations using the finite element software COMSOL for various geometries which have been approximated by the cylindrical or spherical colloidal particle being enclosed by a finite rectangle. The equations are first converted to their weak forms, and entered into the general weak PDE module of COMSOL. None of the COMSOLs special modules are used.

For linear and nonlinear models alike, the computational efficiency is improved by first solving the electrostatic problem, and then the hydrodynamic problem. In time dependent cases, the fluid slip can be averaged and the Stokes problem is solved only once using this averaged slip.
Figure 3-2: Cylinder near a wall in a 10x10 box: (a) Electric field lines. (b) Stokes flow streamlines.

For reasons of completeness and easy reference, here we list the weak forms of the equations solved. This system of equations are converted to a weak form by multiplying by corresponding test functions and integrating over the spatial domain.

The electrical problem turns into

\[ 0 = - \int_{\Omega} \hat{\phi} \nabla^{2} \phi \, dr = \int_{\Omega} \nabla \hat{\phi} \nabla \phi \, dr + \int_{\partial \Omega} \hat{\phi} (n \cdot \nabla \phi) \, ds \]

\[ = \int_{\Omega} \nabla \hat{\phi} \nabla \phi \, dr + \int_{\partial \Omega} \hat{\phi} \partial_{r} q \, dr \]

which is satisfied for all test functions \( \hat{\phi} \). The boundary condition for \( \phi \) is imposed in the form

\[ 0 = \int q (V_{col} - \phi - \zeta) \, dr \]

to be satisfied for all test functions \( q \).

The weak form for the stokes flow is similarly obtained as

\[ 0 = - \int_{\Omega} [\hat{u} \cdot (\nabla \cdot \sigma) + \hat{p} \nabla \cdot \mathbf{u}] \, dr \]

\[ = - \int_{\Omega} [\nabla \hat{u} : \sigma - \hat{p} \nabla \cdot \mathbf{u}] \, dr + \int_{\partial \Omega} \hat{u} \cdot (n \cdot \sigma) \, ds \]

where \( \sigma = \sigma_{H} \) is the hydrodynamic stress tensor. Since we do not have a simple expression
for \( \mathbf{n} \cdot \sigma \), it is best to introduce the new variable (Lagrangian multiplier) \( \mathbf{f} = \mathbf{n} \cdot \sigma \). This is also convenient for calculation of hydrodynamic forces at the surface. Then we obtain

\[
0 = - \int_{\Omega} [\nabla \hat{u} : \sigma - \hat{p} \nabla \cdot \mathbf{u}] \, dr + \int_{\partial \Omega} [\hat{u} \cdot \mathbf{f} + \hat{f} \cdot (\mathbf{u} - \mathbf{u}_s)] \, ds
\]

### 3.3 Isotropic particles near a wall

#### 3.3.1 Cylinder in a DC Field

For isotropic particles near a wall, by symmetry, \( \phi_{cylinder} = 0 \), therefore \( \zeta = -\phi \). Moreover, there is no net horizontal force exerted on the particle, so the only force of interest is in the vertical direction. Another consequence of symmetry is the absence of net torque on the cylinder.

The DC cylinder problem has been solved analytically by Zhao and Bau [199] in the linear case in bipolar coordinates. The mapping between the bipolar and the Cartesian coordinates is given by

\[
x = \frac{c \sin \beta}{\cosh \alpha - \cos \beta}, \quad y = \frac{c \sinh \alpha}{\cosh \alpha - \cos \beta}
\]

where \( \alpha_0 < \alpha < \infty \), and \(-\pi < \beta < \pi\) defines the region outside the cylinder. The geometric constants \( \alpha_0 \) and \( c \) are defined as

\[
\alpha_0 = \text{sech}^{-1}(a/h)
\]

\[
c = \frac{h}{\coth \alpha_0}
\]

(note that there is a typo in the expression for \( \alpha_0 \) in [199]). The hydrodynamic and electrostatic forces on the cylinder are calculated to be

\[
F_H = \frac{2\pi \sinh \alpha_0 E_\infty^2 c}{(\alpha_0 \cosh \alpha_0 - \sinh \alpha_0 \coth \alpha_0) \coth \alpha_0} \times \left\{ \frac{1}{2 \sinh^2 \alpha_0} + \sum_{n=1}^{\infty} \left( \frac{\cosh \alpha_0}{\sinh(n+1)\alpha_0 \sinh \alpha_0} - \frac{1}{\sinh(n+2)\alpha_0 \sinh(n+1)\alpha_0} \right) \right\} \hat{y}
\]

\[
F_E = \frac{2\pi E_\infty^2 h}{\coth \alpha_0} \sum_{n=1}^{\infty} \left( \frac{n^2}{\sinh^2 n\alpha_0} - \frac{n(n+1) \cosh \alpha_0}{\sinh n\alpha_0 \sinh(n+1)\alpha_0} \right) \hat{y}
\]

Because of symmetry, there is no force in the horizontal direction.

We are going to use this solution to gain some confidence in our numerical simulations using COMSOL, some results reported in Fig.3-3. We first used a box of dimensions 20x20 (particle radius being 1), filled with a mesh of maximum edge length equal to 1. We required this mesh to be finer on the cylinder surface by imposing its maximum size to be 0.1 there. The top two in Fig.3-3, we compare the hydrodynamic (left) and the electrostatic (right) forces; and the plots are visually identical. Although the absolute errors remain small, the relative error grows (see bottom subfigures in Fig.3-3) with increasing distance from the wall, possibly because the numerical boundaries (i.e. walls at infinity) start to affect the solution. Experimentation with
Figure 3-3: Validation of numerical simulations for the cylinder near a wall problem. The total hydrostatic (top left), and the electrostatic (top right) forces overlap with the analytical expression of [199] for a mesh of maximum size 0.1 on the cylinder, and maximum global size 1 in a numerical box domain of 20x20 (particle radius being 1). The relative errors of this configuration are plotted and compared with that of a finer mesh (max. size of 0.05 on the cylinder, max. global size of 1) with larger numerical domain (box of 40x40) in the corresponding two bottom plots.

Comsol shows that the hydrodynamic error is sensitive to the size of the box, while the error in the electrostatic force is more sensitive to the mesh size. For a larger box with dimensions 40x40, and twice as finer mesh on the cylinder, we have obtained a similar picture with errors cut to about one third of their values, as shown two bottom subfigures in Fig.3-3.

### 3.3.2 Cylinder in an AC field

As the electric fields are screened quickly by the electrolyte, an AC field is usually preferred. Use of an AC electric field also prevents harmful reactions on electrodes, and enables experimentalists to go to higher applied voltage differences. Such higher voltages may be desirable if they lead to stronger electrokinetic effects of interest.

Far from the wall, the ICEO slip velocity around an ideally polarizable cylinder in an AC field was derived by Squires and Bazant [177], which takes the dimensionless form

\[ \langle u_\theta \rangle = \frac{\sin 2\theta}{1 + \omega^2}. \]
Figure 3-4: The total (a) hydrodynamic (b) electrostatic forces on the cylinder as a function of AC frequency, at distances $h = 0.1ka$, $k = 1, 2, ..., 10$.

We use this expression to calibrate our numerical code, and find excellent agreement far from the wall. This result shows that ICEO flow decays algebraically as $\omega^{-2}$ above the RC charging frequency. Since electrostatic forces do not decay in this limit, we may expect a change in behavior near the wall. At high frequency, there is not enough time for double-layer relaxation, so the electric field resembles that of a conductor in a uniform dielectric medium.

An important observation is that the total hydrodynamic forces vanishes at higher frequencies whereas the total electrostatic force changes sign, but does not vanish. As a result, if the frequency is high enough, there is an equilibrium distance from the wall. This distance decreases as the frequency is increased.

In the high frequency limit, the electrostatic problem approaches the solution of the Dirichlet problem, that is, the laplace equation

$$\nabla^2 \phi = 0$$

combined with the boundary condition

$$\phi = 0 \text{ (on the cylinder)}$$

$$n \cdot \nabla \phi = 0 \text{ (on the wall)}$$

$$\phi = -E_\infty x \text{ (at infinity)}.$$ 

In this case, the solution is given by

$$\phi = \text{Re}(\phi e^{i\omega t}) = \phi \cos \omega t$$
This problem can be solved analytically, and the solution is given by

\[
\phi = 2cE_\infty \sum_{n=1}^{\infty} \frac{e^{-n\alpha_0}}{\cosh n\alpha_0} \cosh n\alpha \sin n\beta - \frac{c \sin \beta}{\cosh \alpha - \cos \beta}
\]

\[
= 2c \sum_{n=1}^{\infty} \left[ \frac{e^{-n\alpha_0}}{\cosh n\alpha_0} \cosh n\alpha - e^{-n\alpha} \right] \sin n\beta
\]

Plugging this into the electrostatic force leads to the formula

\[
F_{E,\omega \to \infty} = -2\pi cE_\infty \sum_{n=1}^{\infty} \left( \frac{n^2}{\cosh^2 n\alpha_0} \right) + \frac{n(n+1) \cosh \alpha_0}{\sinh n\alpha_0 \sinh (n+1) \alpha_0}
\]

with the same notation as in Zhao and Bau [199].

3.3.3 Sphere in an AC field

ICEO flow around a sphere was first considered by Gamayunov et al. [64]. Following the cylinder analysis of Squires and Bazant [177], it is straightforward to derive the (dimensionless) ICEO slip velocity around an ideally polarizable sphere in an AC field, far from the wall,

\[
\langle u_\theta \rangle = \frac{9}{16} \frac{\sin 2\theta}{1 + (\omega/2)^2}
\] (3.8)
Note that since \( (\cos^2 \omega t) = 1/2 \) the ICEO flow in a true DC field \( E_\infty \) is twice as large as the time-averaged flow in an AC field \( E_\infty \cos \omega t \) in the low frequency or DC limit \( \omega \to 0 \). We will prefer reporting quantities for the DC limit throughout this chapter.

In the DC limit, the hydrodynamic and electrostatic forces on a sphere near a wall show qualitative similarity with that of a cylinder. As shown in Fig.3-6, both forces are repulsive and decay as the sphere moves away from the plane. Note that the magnitude of hydrodynamic forces are about 2 orders of magnitude larger than the dielectric forces.

The results start to differ from the cylinder problem for the case of real AC forcing, however. Shown in Fig.3-7 are the hydrodynamic and electrostatic forces as a function of AC frequency for a sphere at various distances from the wall. While the hydrodynamic forces quickly drop to zero at high frequencies, the electrostatic forces persist and even increase at high frequencies, unlike the cylinder problem. Since both forces are repulsive, there is no equilibrium plane attracting the spherical particle, which is repelled to infinity by the wall regardless of the forcing frequency. This is true even when a Stern layer is introduced into the double layer model.

3.4 Janus sphere near a wall

3.4.1 Broken symmetries

Without a nearby wall, a Janus sphere would align itself perpendicular to the electric field, that is, some of the electric field lines would be included in the plane dividing the Janus particles metal and insulating sides, as sketched in Fig.3-8. This effect has been demonstrated in [178], and is presumably stronger than the wall effects, at least when the particle is sufficiently far from the wall. That being said, we will assume that the particle always stays in the described configuration, that is, with its dividing plane aligned with the electric field. This is not to say that the particle has no room for different rotational configurations, it can still rotate around \( x \) and \( y \) axis. By symmetry, there is no rotation about the \( y \) axis, so we are left with rotations.
Figure 3-7: The (a) hydrodynamic and (b) electrostatic forces on a full metal sphere as a function of frequency at the distances $h = 2a, a$, and $a/2$ away from the wall.

Figure 3-8: Sketch of basic Janus particle motion, as demonstrated in [178]: (a) Janus particles would align themselves with the electric field (b) once they are aligned, they would translate towards their insulating side.
only around the \( x \)- axis. This is much easier to deal with than the original problem though, as only one angle is enough to describe the particle's orientation.

Far from the wall, the bulk velocity perpendicular to a DC field in the stable orientation is given by the formula of Squires and Bazant [178] (Eq. 3.16), which takes the dimensionless form,

\[
U_{DC} = \frac{9}{64} = 2(U_{AC}(\omega \rightarrow 0))
\]  

(3.9)

neglecting compact-layer surface capacitance. As noted above, the time-averaged velocity in a sinusoidal AC field is smaller by a factor of two in the limit of zero frequency. Even in the bulk, without a wall, it is difficult to solve analytically for the ICEO flow at finite AC frequency around a Janus particle, since the electrical response is not simply an induced dipole, due to the broken symmetry. Nevertheless, we will argue that the frequency dependence of the flow is similar to that around a sphere (3.8), constant below the RC charging time and decaying above it.

For a Janus sphere aligned perpendicular to the electric field near a wall, a crucial observation is that the \( y \)-symmetry breaks down. As a result, there is a net force in the \( y \)-direction, as well as a net torque in \( x \)-direction. The former leads to translation parallel to the wall, while the latter causes rotation of the dielectric face toward the wall. We shall see that these effects of broken symmetry completely change the behavior near wall in an AC or DC field: Although a polarizable sphere is always repelled to infinity by an insulating wall, a Janus particle is always (eventually) attracted to it.

### 3.4.2 Basic mechanism for wall attraction

The key new effect is rotation due to hydrodynamic torque caused by asymmetric ICEO flow near the wall. This generally causes the Janus particle to be attracted to the wall, as shown in figure 3-10. The physical mechanism can be understood as follows. When the field is first
Figure 3-10: Sketch of ICEO flows $u$ and resulting ICEP torques $T$ which cause a Janus particle to tilt its less polarizable end toward a wall, while translating toward the wall (until stopped by double-layer overlap) and perpendicular to the applied AC field $E$ (directed into the page and parallel to the wall). This physical mechanism may explain why the transverse ICEP motion of Janus particles was observable over the surface of a glass wall in the experiments of Gangwal et al. [65].

turned on, the Janus particle quickly rotates, by ICEP and DEP, to align its metal/insulator interface with the field axis, but with an arbitrary azimuthal angle, mainly set by the initial condition. As described by Squires and Bazant [178], the ICEO flow around the particle draws in fluid along the field axis and ejects it radially at the equator – but only on the polarizable hemisphere, which acts like a “jet engine” drives ICEP motion in the direction of the non-polarizable hemisphere, which leads the way like a “nose”.

Near a wall, as shown in the figure, the outward ICEO flow pushes down on the wall harder on the side of the polarizable “engine” than on that of the non-polarizable “nose”, which produces a hydrodynamic torque tilting the nose toward the wall. A second cause of this rotation is the hydrodynamic coupling between ICEP translation parallel to the wall and rotation by shear stresses to cause rolling past the wall. Regardless of the initial position, these two sources of ICEP rotation cause the nose to eventually face the wall, so that the translational engine drives it toward the wall. This is likely the origin of the counter-intuitive attraction of Janus particles to a glass wall in the experiments of Gangwal et al [66].

What happens next depends on the details of the particle-wall interaction at very close distances. We will see that the bulk model with thin double layers must eventually break down, since the particle either collides with the wall or gets very close to it, leading to overlapping particle and wall double layers. It is beyond the scope of this work to accurately treat the nonlinear and time-dependent behavior of these overlapping double layers, so we will explore two models: (i) a cutoff “collision” height, where overlapping double layers stop any further motion toward the wall, while still allowing transverse motion, (ii) a compact layer model with $\delta = 10$. Both cases use infinitely thin double layer approximation, that is, no overlapping double layers. The model (i) can be justified by the fact that, in the experiments [66], that the particles
Figure 3-11: In the DC limit (ω → 0), we plot (a) horizontal velocity (b) vertical velocity and (c) tilting speed (degrees per unit displacement time τ) as a function of the tilt angle θ for the Janus particle at distances h = 0.5a and h = 0.05a from the wall.

and walls have equilibrium surface charge of the same sign. For concreteness, we will simulate Model (i) with a cutoff height h = λ = 0.05a, e.g. corresponding to a double-layer thickness (screening length) of λ = 50nm with particles of size a = 1μm.

Based on examples above, we expect a subtle dependence on the AC frequency. Electrostatic DEP motion will always begin to dominate the hydrodynamic ICEP motion at high frequency. Therefore, we now consider the low and high frequency cases separately.

### 3.4.3 Dynamics as a function of AC frequency

As shown in Fig. 3-12, in the low frequency limit, the Janus particle experiences a rotational velocity turning its non-polarizable side toward the wall, as explained above. The hydrodynamic ICEP torque is orders of magnitude larger than the electrostatic DEP torque, until the particle gets quite close to the wall. The magnitude of the horizontal ICEP velocity $U_y$ parallel to the surface and perpendicular to the field is close to its bulk value $U_y = 9/128 \approx 0.07$ even fairly close to the wall at a height $h = 0.5a$ at zero tilt, but reduces with the tilt angle. For small tilt angles and close to the wall at $h = 0.05a$, the horizontal velocity increases to $U_y \approx 0.10$, but it drops below the bulk value at larger tilt angles, e.g. to $U_y \approx 0.05$ at $\theta = 45$ degrees. Below we will see that this velocity is further reduced at higher forcing frequencies, due to the reduction of ICEO flow (since DEP cannot contribute to motion perpendicular to a uniform field).

If compact layer is absent, i.e. $\delta = 0$, in the DC limit the particle moves ever closer to the wall regardless of the orientation since $U_z < 0$ for any tilting of the nose toward the wall. Even if the vertical motion is artificially stopped at a critical height, the rotation continues in the DC limit until the particle points its non-polarizable nose directly at the wall ($\theta = 90$) and the motion stops, although this can take a long time, since the rotation slows down substantially.
Figure 3-12: Typical trajectory of a Janus particle under the DC limit $\omega \to 0$ interacting with the wall: As a function of time, plotted are (a) Tilt angle (b) Distance from the wall (c) The horizontal speed. Also, we plot the distance from the wall as a function of horizontal position in (d).
for tilt angles larger than 45 degrees. As discussed below, a number of effects might lead to such a stabilization of the tilt angle, thus allowing steady translation along the wall.

As shown in Fig. 3-12, a typical simulated trajectory of the Janus particle shows it translating perpendicular to the field while rotating and attracting to the wall, until eventually coming to rest facing the wall. Even when the particle’s motion stops, however, its polarizable hemisphere (“engine”) continues driving a steady ICEO flow, which can lead to long-range hydrodynamic interactions with other particles. This is an interesting theoretical prediction which should be checked in experiments. Such immobilized Janus particles may have interesting applications in microfluidics.

Similar behavior is predicted for finite AC frequencies in many cases. In particular, if a particle is initially mostly facing its non-polarizable hemisphere toward the wall (θ near 90°), it will swim toward the wall and come to rest, as in the DC limit of Figure 3-12.

There are some new effects in AC fields, however, since ICEO flows are suppressed with increasing frequency. The competing effect of DEP can prevent the Janus particle from fully rotating and coming to rest on the surface, at least in Model (i) where the collision is prevented artificially, as shown in Figure 3-15. At ω = 1 (the characteristic RC frequency of the particle), the rotation slows down substantially beyond 45° but does not appear to stop (not shown). In this regime the horizontal velocity decays to $U_y \approx 0.015$. For ω = 10 the particle appears to settle down to an equilibrium tilt angle around 45°, while steadily translating over the wall. The limiting horizontal velocity is roughly $U_y \approx 0.009$.

### 3.4.4 Compact Layer Effects

At electrolyte interfaces, a compact layer also forms due to the adsorption of the solvent molecules and ions to the surface. The simplest theory for this compact layer is to assume a charge
Figure 3-14: For AC frequency (ωτ_c = 10), we plot (a) horizontal and vertical velocities and (b) tilting speed as a function of the tilt angle θ for the janus particle at distances h = 0.5a and h = 0.05a from the wall.

Figure 3-15: Typical trajectory of a janus particle under AC frequency ωτ_c = 10 interacting with the wall: As a function of time, plotted are (a) Tilt angle (b) Distance from the wall (c) The horizontal speed. Also, we plot the distance from the wall as a function of horizontal position in (d).
Figure 3-16: Equilibrium distance from the wall for a Janus particle directly facing it with its insulating side, as a function of $\delta$, a measure of Stern layer capacitance.

free region (which may consist of adsorbed solvent molecules) of a certain thickness that acts as a capacitance in series with the diffuse layer. This Stern layer model is crucial in explaining the behaviour of the double layer capacitance when used with the Gouy-Chapman theory, which alone has unphysical predictions in the large voltage regime.

In electrophoresis, the Stern layer model has usually been used to explain the discrepancy between the mathematical predictions with the experimental data. If $\delta = \lambda_S/\lambda_D$ is the ratio of the thicknesses of the compact layer and the Debye length as usual, the zeta potentials as well as the hydrodynamic slip are reduced by the factor $1 + \delta$. This results in a proportional decrease in the resulting hydrodynamic flow, which gives the main contribution to particle motion.

Without a compact layer, the predicted electrophoretic velocities are larger than the measured ones. Therefore (a positive) $\delta$ can be chosen to rescale the calculated quantities to match with the experiment. However, the compact layer model is more than just a simple scaling by $1/(1 + \delta)$, because: (i) the electrostatic forces and motion induced by them are unaffected, (ii) the charging time and the characteristic AC frequency are also rescaled by $1/(1 + \delta)$.

In our model, the compact layer enables us to predict an equilibrium distance from the wall. For the particle facing the wall, there are two factors competing with each other; the hydrodynamic propulsion towards the wall and the electrostatic interaction pushing away from the wall. Both forces get stronger as the particle approaches the wall, as well as the ratio $F_E/F_H$ of electrostatic force to hydrodynamic force. Still, even at small distances ($h = 0.05a$) from the wall, the attractive hydrodynamic force is 5-6 times larger than the repulsive electrostatic force.

Therefore the theory predicts that the particle eventually collides with the wall, which is contrary to what is observed in the experiments [66]. However, if we assume there is a compact layer with large enough $\delta$, the hydrodynamic attraction can be made as small as the opposing
Figure 3-17: Typical trajectory of a janus particle interacting with the wall in the limit $\omega \rightarrow 0$, with a compact layer of $\delta = 10$: As a function of time, plotted are (a) The horizontal speed (b) Distance from the wall (c) Tilt angle. Also, we plot the distance from the wall as a function of horizontal position in (d).

electrostatic forces, and there exists an equilibrium distance for the particle. This equilibrium distance is an increasing function of $\delta$, and it is plotted in Fig. 3-16.

As shown in Fig. 3-16, there is an equilibrium distance $h > 0.05a$ for the particle for $\delta > 5.7$ (simulations with smaller $h$ are not well resolved). A choice of $\delta$ around 7-10 also helps us match the calculated horizontal electrophoretic velocities to experimentally measured values. Therefore the compact layer model explains the equilibrium distance from the wall while predicting particle velocities consistent with the experiment.

3.4.5 Comparison to experiment

Our simulations are in reasonable agreement with the experimental observations of Gangwal et al [66] for metallo-dielectric Janus particles in dilute NaCl solutions in the low-frequency regime $\omega < 1$. The bulk theory of Squires and Bazant (3.9) accurately fits the experimental velocity as a function of the field strength (Fig. 3 of Ref. [66]) and the particle size (Fig. 4), if $\delta = 10$, $U_{expt} = (9/128)/(1 + 10) = 0.006$. This $\delta$–value is somewhat larger than that inferred from prior experiments on ICEO flow in dilute KCl around a larger (100 $\mu$m radius) platinum cylinder [108], but it is also observed that the ICEP velocity is slower than predicted at larger sizes (Fig. 4 of Ref. [66]). In addition, Gangwal et al [66] observed only the ICEP motion very close to the walls.

Our simulations predict that the particles are quickly attracted to the walls over a time of order the channel width (60 $\mu$m) divided by the typical ICEP velocity (1 $\mu$m/s), which is
roughly one minute, consistent with experimental observations. The particles are also predicted to tilt, and moderate tilt angles can also be inferred from experimental images, although more accurate measurements are needed. If the tilt angle stabilizes around 45° (see below), then the simulations (Fig. 3-12) predict that the ICEP translational velocity should be only 0.05/0.07 = 70% of the bulk value close to the wall, which would imply the slightly smaller value δ = 7.

Apart from the rotational dynamics, therefore, the theory is able to predict the ICEP velocity fairly well.

Without stopping the rotation artificially, we are able to predict the experimentally observed steady motion along the wall only at moderate to large ω. The reduction of ICEO flow in this regime reduces hydrodynamic torque (see below) and also enhances the effect of stabilizing electrostatic forces. Although $U_{\text{cepf}} = 0.006$ is measured in the low-frequency plateau $\omega < 1$, this behavior otherwise seems quite consistent, since the slower ICEP velocity can also fit the experimental data using smaller (and perhaps more reasonable) values of δ. For example, the predicted velocity of $U = 0.015$ at $\omega = 1$ implies $\delta = 1.5$, while the velocity $U = 0.009$ at $\omega = 10$ implies $\delta = 0.5$.

The difficulty in predicting the stable tilt angle at low frequency may be due to our use of the low-voltage, dilute-solution theory, which generally overpredicts the magnitude of ICEO flows, especially with increasing salt concentration. For example, the electrophoretic mobility can saturate at large induced voltages, and the charging dynamics can also be altered significantly when crowding effects are taken into account [11]. As a result, our simulation results at moderate frequencies $\omega = 1 - 10$, which exhibit reduced ICEO flow due to incomplete double-layer charging, may resemble the predictions of more accurate large-voltage, concentrated-solution theories at low frequency $\omega < 1$, where flow is reduced instead by ion crowding in the double layer. This will be the subject of future work.

### 3.4.6 Contact mechanics

Another source of error in the model is our inaccurate treatment of the contact region, where double-layers may overlap. We have simply used the bulk concentration model for all our simulations, but there may be more complicated mechanical effects of the contact region. In particular, there may be enhanced hydrodynamic slip, due to the repulsion of overlapping (equilibrium) double layers of the same sign, as in the experiments.

By examining the forces and torques close to the wall, we can infer to some degree what mechanical properties of the contact region might lead to the observed ICEP sliding along the wall and smaller tilt angles at lower frequencies (and thus also somewhat larger velocities). As shown in Fig. 3-18, before the particle gets very close to the wall, the (mostly hydrodynamic) torque acts to completely tilt the non-polarizable face toward the wall leading to collision. As noted above in Fig. 3-10, this can be understood as a result of the downward component of ICEO flow on the polarizable hemisphere raising the pressure by pushing on the wall on that side.

The situation changes when the particle gets very close to the wall. As shown in Fig. 3-18, the torque changes sign at a tilt angle which is roughly 45°. This again can be understood from Fig. 3-10, since the ICEO flow between the particle and the wall on the polarizable side, which drives the torque, is mostly absent. It would thus seem that even in a DC field, the particle would not rotate any further, but this thinking neglects the hydrodynamic coupling between
Figure 3-18: Torque on a fixed Janus sphere versus tilt angle at heights $h = 0.5a$ and $0.05a$ when (a) $\omega \to 0$ (b) $\omega \tau_c = 10$.

Figure 3-19: Horizontal force on a fixed Janus sphere versus tilt angle at heights $h = 0.5a$ and $0.05a$ when (a) $\omega \to 0$ (b) $\omega \tau_c = 10$. 
translational force and rotational velocity near the wall, Eq. (3.4). In Fig. 3-19, we see that the force on the particle parallel to the wall $F_y$ remains strong, and this leads to a rolling effect over the wall due to shear stresses. For this reason, the rotational velocity persists in Fig. 3-12 even when the torque goes to zero in Fig. 3-18.

The model assumes no slip on all non-polarizable surfaces, but this may not be a good approximation near the contact point when double layers overlap. If the equilibrium surface charges (or zeta potentials) on the non-polarizable hemisphere and the wall have opposite signs, then the overlapping double layers lead to a strong attraction, which would only stiffen the effective contact with the surface, and thus only increase the viscous rolling effect during motion along the surface. If the equilibrium surface charges (or zeta potentials) have the same sign, however, as in the experiments on gold-coated latex Janus particles near glass walls [66], then there is a strong repulsion at the contact point. This repulsion stops the collision with the wall in Model (i), but it may also “lubricate” the contact and allow for some sliding. This effective slip over the wall near the contact point could reduce the viscous rolling, and, in the absence of torque, cause the rotation to stop, or at least be reduced for tilt angles above 45°. In that case, we might expect a more accurate model of the contact region to predict the experimentally observed motion, sliding over the surface by ICEP with a small tilt angle ($\theta < 45^\circ$), for a wider range of conditions, including lower AC frequency, perhaps even in the DC limit.

### 3.5 Conclusion

We have used the existing low-voltage theory of ICEP to predict the motion of polarizable particles near an insulating wall. Our results for symmetric spheres and cylinders confirm the expected repulsion from the wall due to ICEO flow, sketched in Figure 1(a). In the case of the cylinder we show that attraction is also possible at high frequency, where DEP from electrostatic forces dominates slip-driven ICEP motion.

Our results for asymmetric Janus particles reveal an unexpected attraction to the wall by a novel mechanism illustrated in Figure 3-10, which involves tilting of the less polarizable face toward the wall. Once it reaches the wall, if double-layer repulsion prevents further collision, the particle either rotates completely and ceases to move, while driving steady ICEO flow, or reaches an equilibrium tilt angle around 45° while steadily translating along the surface, perpendicular to the electric field. The latter motion only arises at moderate frequencies in our model, above the characteristic charging frequency for the double layers, while in experiments it is also observed at low frequencies. More accurate models taking into account reduced ICEO flow at large voltage in non-dilute solutions and more accurate models of the contact region may improve the agreement with experiments.

In any case, we have shown that polarizable particles can display complex interactions with walls due to broken symmetries in ICEO flows. Attractive and repulsive interactions can be tuned by varying the geometry of the particles (and the walls), as well as the AC frequency and voltage. These phenomena may find applications in separations and self-assembly of colloids or in local flow generation in microfluidic devices.
Chapter 4

Steric Effects on Diffuse-Charge Dynamics

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4.1 Introduction

In this and the next chapter, we develop a simple analytical theory for the dynamics of electrolytes, taking into account steric effects of finite ion size. Motivated by recent experiments in microfluidics, microbatteries, and electrochemical sensors, our motivation is to describe the response of an electrolyte to an applied voltage of several volts, which is large enough to cause crowding of ions near a surface, even if the bulk solution is very dilute and in the absence of surface reactions. The ions thus lose their classical Poisson-Boltzmann distribution, which has major implications for their dynamics.

As a guide to the reader, we summarize the main results. The present chapter begins in this section with a historical review of dilute solution theory, its limitations at large voltages, and attempts to account for steric hindrance, specific interactions, and many-body electrostatics. As a first approximation, we focus only on steric effects, and analyze the dynamical response of a thin diffuse layer to a large applied voltage, using two simple continuum models (section 4.2). The key results, common to both steric models, are: (i) the diffuse layer’s differential capacitance is bounded and decreases at large voltage (section 4.3), and (ii) it cannot easily engulf enough ions to perturb the bulk concentration or conduct significant tangential currents (section 4.4). These predictions are completely opposite to those of dilute solution theory (based on the Gouy-Chapman model of the diffuse layer). In chapter 5, we propose general, time-dependent equations with steric constraints and revisit the parallel-plate charging problem in more detail.

4.1.1 Dilute solution theory

For the past century, dilute solution theory has provided the standard model of electro-diffusion of ions [158, 133, 113] and electrokinetic phenomena [115, 89]. The fundamental assumption is
that the chemical potential of a point-like ion \(i\) in a dilute solution has the simple form,

\[
\mu_i = kT \ln c_i + z_i e\psi
\]  \hspace{1cm} (4.1)

where \(z_i e\) is the charge, \(c_i\) the concentration, and \(\psi\) the electrostatic potential, determined in a mean-field approximation by Poisson’s equation,

\[
-\nabla \cdot (\varepsilon \nabla \psi) = \rho = \sum_i z_i e c_i.
\]  \hspace{1cm} (4.2)

typically with a constant permittivity \(\varepsilon\). The form (4.1) is sometimes called the “ideal” component of the chemical potential [69], to which various “excess” components at finite concentration can be added (see below).

In many situations, it is assumed that the ions are in quasi-thermal equilibrium with a Boltzmann distribution,

\[
c_i = c_i^0 e^{-z_i e\psi/kT}
\]  \hspace{1cm} (4.3)

with a reference concentration \(c_i^0\), in which case Equation (4.2) reduces to the Poisson-Boltzmann equation (PB). For example, to analyze a thin double layer, it is natural to choose \(c_i^0\) to be the concentration of species \(i\) in the nearby neutral bulk solution. In most situations, the PB equation is hard enough to solve that the Debye-Hückel linearization for small potentials, \(\psi \ll \psi_T\), is required for analytical progress, where \(\psi_T = kT/z_i e\) is the thermal voltage (\(\approx 25\) mV for monovalent ions at room temperature).

The well known exception, which admits a simple solution, is the case of a symmetric binary \(z : z\) electrolyte in a 1D geometry, where the PB equation in the form

\[
\varepsilon \frac{\partial^2 \psi}{\partial x^2} = 2ze c_0 \sinh \left(\frac{ze\psi}{kT}\right)
\]  \hspace{1cm} (4.4)

was solved analytically by Gouy [73] and Chapman [40] (GC) for a semi-infinite electrolyte of bulk concentration \(c_0 = c_i^0 = c_j^0\) near a flat charged surface [133, 113, 89]. (It is less well known that Gouy [73] also solved the case of an asymmetric \(2z : z\) electrolyte.) Although this solution may seem quite special, it describes the most common situation where diffuse charge is confined to a thin capacitor-like “double layer” near a solid surface. The width of the diffuse layer is the Debye [47] (or, more properly, Gouy [73]) screening length,

\[
\lambda_D = \sqrt{\frac{\varepsilon kT}{2z^2 e^2 c_0}}
\]  \hspace{1cm} (4.5)

as can be seen by scaling (4.4) with \(\tilde{x} = x/\lambda_D\) and \(\tilde{\psi} = \psi/\psi_T\) to obtain the dimensionless form, \(\psi'' = \sinh \tilde{\psi}\). The screening length (\(\lambda_D \approx 1 - 100\) nm in aqueous electrolytes) is typically much smaller than any geometrical length, so the bulk solution remains quasi-neutral with the diffuse charge confined to thin, locally flat, quasi-equilibrium double layers.

Due to its analytical simplicity and wide applicability, the Gouy-Chapman solution has become the standard model for highly charged double layers. It is the basis for the classical theory of tangential “surface conduction” through the diffuse layer [19, 20, 48, 52], as well as the recently noted phenomenon of salt “adsorption” (or “uptake”) from the neutral bulk by the
diffuse layer in response to a large applied voltage [13, 45]. Such predictions of the GC model have major implications for electrokinetic phenomena of the first kind, such as electro-osmosis, electrophoresis, streaming potential, and diffusiophoresis, at large surface potentials [115, 89].

Dilute solution theory has also been used in nearly every model of diffuse charge during the passage of current. Near equilibrium, the flux density of ion $i$ is proportional to the gradient of its chemical potential (4.1),

$$ F_i = -b_i c_i \nabla \mu_i = -D_i \left( \nabla c_i + \frac{z_i e}{kT} c_i \nabla \psi \right) $$

where Einstein’s relation, $D_i = b_i / kT$, relates the ion’s mobility $b_i$ to its diffusivity $D_i$. For a system in quasi-steady state, $\nabla \cdot F_i = 0$, the nonzero current, $J = \sum_i z_i e F_i$, only slightly perturbs the Boltzmann distribution of the ions. As a result, the GC solution is also widely used to describe diffuse-layer effects on electrode reaction kinetics [133, 10] (the Frumkin correction [62]), up to Nernst’s limiting current, where the bulk concentration of an electro-active species vanishes. At larger “superlimiting” currents, the PB equation loses validity, but dilute-solution theory is still used to describe diffuse charge, which loses its Boltzmann distribution [175] and extends into the bulk as “space charge” [159], while retaining an inner boundary layer at the screening length [43]. The dilute-solution space-charge model is the basis for theories of electrokinetic phenomena of the second kind, such as super-fast electrophoresis [51] and hydrodynamic instability at a limiting current [160].

Dilute solution theory has also been used to describe the dynamics of electrolytes, subject to time-dependent applied voltages. The classical description comes from the Poisson-Nernst-Planck equations (PNP), which consist of Eq. (4.2) and mass conservation laws for the ions,

$$ \frac{\partial c_i}{\partial t} = -\nabla \cdot F_i = D_i \left[ \nabla^2 c_i + \frac{z_i e}{kT} \nabla \cdot (c_i \nabla \psi) \right] $$

where $D_i = \text{constant}$ is normally assumed. Again, general solutions are only possible upon linearization, where the potential satisfies the Debye-Falkenhagen equation [47]. In the nonlinear regime, for thin double layers, the GC solution again holds since the diffuse-charge remains in quasi-equilibrium, and the diffuse-layer acts like a voltage-dependent differential capacitance in series with a bulk resistor [118]. Such equivalent circuit models can be derived systematically from the PNP equations by asymptotic analysis, which also reveals corrections at large voltages, due to bulk diffusion in response to salt adsorption [13] and surface conduction [45] at large applied voltages. Such nonlinear diffuse-layer effects could be important in interpreting impedance spectra in electrochemical sensing [119, 68], or in understanding high-rate thin-film rechargeable batteries [50, 193, 131, 184].

Another current motivation to study nonlinear diffuse-charge dynamics comes from “induced-charge” electrokinetic phenomena [12]. The preceding models of double-layer relaxation have been used extensively in theories of AC pumping of liquids over electrode arrays [146, 1, 72, 32, 145, 9], induced-charge electro-osmotic flows around metallic colloids [64, 126] and microstructures [177, 108, 9], and dielectrophoresis [165, 170, 178] and induced-charge electrophoresis [12, 195, 178, 162] of polarizable particles in electrolytes, although a nonlinear analysis based on the PNP equations has not yet been attempted for any of these situations. This may be a good thing, however, since we will show that dilute solution theory generally breaks down in the regime of experimental interest, where the applied voltage is much larger than the thermal
voltage, \( V > \psi_T \).

### 4.1.2 Validity of the nonlinear model for dilute solutions

Dilute solution theory provides a natural starting point to understand nonlinear effects in electrolytes, and the GC model is used in all of the examples above to model the diffuse layer at large applied potentials. In spite of its mathematical appeal, however, nonlinear dilute solution theory has limited applicability, due to the exponential sensitivity of the counter-ion concentration to voltage. For example, in the typical case of quasi-equilibrium, the Boltzmann factor (4.3) brings nonlinearity to the PB equation (4.4) when \( \psi > \psi_T \), but this dependence is so strong that the surface potential cannot get much larger without invalidating the assumption of a dilute solution.

To see this, note that there must be a maximum concentration, \( c_{\text{max}} = a^{-3} \), of counterions packed with typical spacing \( a \) near a highly charged surface. This effective ion size is clearly no smaller than the ionic radius (typically \( \approx 1\text{Å} \)), although it could be considerably larger (several nm), taking into account hydration effects and ion-ion correlations, especially in a large electric field. For the sake of argument, consider a very dilute bulk solution, \( c_0 = 10^{-5}\text{M} \), with \( a = 3\text{Å} \) and \( z = 1 \). The nonlinear regime begins at a diffuse-layer potential \( \Psi_D \approx kT/ze = 25 \text{ mV} \), but the steric limit is reached in dilute solution theory at \( \Psi_c \approx 13kT/ze = 330 \text{ mV} \), where

\[
\Psi_c = -\frac{kT}{ze} \ln(a^3 c_0) = \frac{kT}{ze} \ln \left( \frac{c_{\text{max}}}{c_0} \right). \tag{4.8}
\]

Since the solution ceases to be “dilute” well below the steric limit, there is only a narrow window of surface potentials \( \approx 25 \text{ – 200 mV} \), sometimes called “weakly nonlinear regime” [13], where nonlinearity arises and the fundamental assumption (4.1) remains valid.

Unfortunately, the most interesting predictions of the non-linear PB theory tend to be in the “strongly nonlinear regime”, where the dilute approximation fails dramatically. For example, the Dukhin number, which controls the relative importance of tangential conductivity in a thin diffuse layer, \( \sigma_s \), compared to bulk conductivity, \( \sigma \), at a geometrical scale \( L \), has the following form [19, 20, 48],

\[
\text{Du} = \frac{\sigma_s}{\sigma L} = 4 \frac{\lambda_D}{L} \sinh^2 \left( \frac{z e \Psi_D}{4kT} \right), \tag{4.9}
\]

assuming the Gouy-Chapman model. This is also the dimensionless ratio, \( \Gamma_s/c_0 L \), of the excess surface concentration of ions, \( \Gamma_s \), relative to the bulk concentration, so it also governs the (positive) adsorption of neutral salt from the bulk in response to an applied voltage [13, 116]. The general derivation of Eq. (4.9) assumes a thin double layer [45], but in that case \( \lambda_D \ll L \) a large Dukhin number corresponds to situations where the steric constraint is significantly violated, \( \Psi_D > \Psi_c \), rendering Equation (9) inappropriate. Similar concerns apply to other nonlinear effects in Gouy-Chapman theory, such as the rapid increase of the differential capacitance (defined below) with surface potential,

\[
C_D = \frac{\varepsilon}{\lambda_D} \cosh \left( \frac{z e \Psi_D}{2kT} \right), \tag{4.10}
\]

which would have important implications for electrochemical relaxation around conductors [169,
4.1.3 Beyond the Poisson-Boltzmann picture

We are certainly not the first to recognize the limitations of dilute solution theory. Historically, concerns about the unbounded capacitance of a thin diffuse layer in the GC solution (4.10) first motivated Stern [180] to hypothesize that there must also be compact layer of adsorbed ions on the surface, as originally envisioned by Helmholtz [80]. The Stern layer is where electrochemical reactions, such as ion dissociation (setting the equilibrium charge on a dielectric) and/or redox couples (setting the Faradaic current at an electrode), are believed to occur, within a molecular distance of the solid surface [113, 115]. The Stern layer capacitance (see below) helps to relieve the overcharging of the diffuse layer in Gouy-Chapman theory, but, due to steric constraints, it too cannot conceivably withstand a voltage much larger than $\psi_c$. Instead, at larger voltages, the region of ion accumulation must inevitably extend away from the surface into the solution, where ions undergo hindered transport in a concentrated solution without having specific interactions with the solid.

The most basic aspect of a concentrated solution is the finite molecular length scale, $a_0$. Bikerman in 1942 [21] was perhaps the first to give any treatment of volume effects in the diffuse layer, after Stern's model in 1924 did so only via a very crude cutoff monolayer at the surface. Regarding the Stern model, Bikerman wrote "the idea of special properties of monomolecular layers has lost much of its appeal since 1924", but this trend was later reversed in a big way. Ironically, it is Stern's model which is widely used today, while Bikerman's original MPB approach has been mostly lost and reinvented at least five times afterwards.

In 1950, Dutta and Bagchi [6, 54] in India did the first derivation of a modified PB model starting from a lattice model and derived Fermi-like statistics. Their theory was further developed by Wicke and Eigen, and Freise [194, 60, 55] in the 1950s. After being forgotten for almost half a century, it was reinvented and extended in the past decade by Iglic and Kral-Iglic [90, 103, 26, 25] and Borukhov, Andelman, and Orland [29, 30, 28]. These authors proposed free energy functionals, based on continuum (mean-field) approximations of the entropy of equal-sized ions and solvent molecules, which they minimized to derive modified Poisson-Boltzmann equations (MPB). The motivation for this work was mainly to address the effect of large ions, whose sizes may be comparable to the screening length, in an equilibrium diffuse layer with $\Psi_D \approx \psi_T$. Our main point here is that crowding effects can also be very important for small ions near a polarizable surface, when subjected to a "large" voltage the exceeding the threshold $\psi_c$. No matter how dilute is the bulk solution, a sufficiently large electric field can always draw enough ions to the surface to create a concentrated solution in the diffuse layer. Finally, the MPB model was independently applied to dynamics at large voltages by Kilic et al. [98, 99] (and by this thesis) in the USA and to ionic liquids by Kornyshev [102] in England in 2007. Kilic, Bazant and Ajdari [99] (as well as this thesis) gave the first extension to time-dependent MPNP equations, and showed that for a thin flat double layer, very similar results can be obtained from a "composite diffuse layer model" with a uniform condensed layer patched to an outer PB layer.

There have also been attempts to go beyond the mean-field approximation of steric effects, by treating specific (and in some cases also Coulombic) ion-ion and ion-wall interactions. Simple MPB equations have been proposed, which modify the charge density to account for the spatial
correlation function between an ion in solution and a flat wall (via an effective external potential) based on molecular dynamics simulations [61, 142, 91], but such models are not easily extended to other geometries, such as a rough wall [100]. Corrections of this type can also be obtained from a general probabilistic model of interacting ions, whose dynamics are given by nonlinearly coupled Langevin equations. Using this approach, Schuss, Nadler and Eisenberg rigorously derived “conditional PNP” (and PB) equations where each ion concentration \(c_i(r)\) in the mean-field Poisson's equation (4.2) is replaced by the conditional probability density of finding an ion at a certain position, given the positions of the other ions [164, 128, 129], although a simple closure of the model requires further assumptions about statistical correlations.

There are a variety of general statistical mechanical approaches from liquid state theory [81], which have been applied to electrolytes, taking into account not only steric effects, but also many-body electrostatic correlations (see below). Since the 1970s, the modest, but challenging, goal has been to accurately predict the equilibrium distribution of ions in Monte Carlo simulations of the “primitive model” of charged hard spheres in a homogeneous dielectric continuum bounded by a hard, charged wall. Typically, the model is studied in the limit of “small” surface potentials (\(\Psi_D \approx kT/e\)) relevant for equilibrium surfaces. For example, a plethora of MPB equations (such as “MPB4", “MPB5",...) perturbing Gouy-Chapman theory have been derived by variations on the Mean Spherical Approximation [106, 138, 38, 139, 140, 39, 17]. More complicated, but often more accurate, theories have also been derived using statistical Density Functional Theory (DFT) [70, 71, 148]. By writing the ion flux as the gradient of an electrochemical potential obtained from the DFT free energy functional [69] (as we do in chapter 5, using the much simpler functional of Borukhov et al. [29]), it has been shown that the selectivity of ion channels can be understood to a large extent in terms of entropic effects of charged hard spheres [157].

In spite of many successes and the appealing first-principles nature of liquid-state theories, however, they are not ideally suited for our purpose here of capturing time-dependent, large-voltage effects in a simple model. Liquid-state theories are not analytically tractable and thus not easily coupled to macroscopic continuum models, although perhaps empirical fits could be developed for quantities of interest. For example, the DFT approach requires nontrivial numerical methods, just to evaluate the steady flux in a one-dimensional ion channel [69, 157]. Another concern is that liquid-state theories have been designed and tested only for “small” voltages (\(\Psi_D \approx kT/e\)) at equilibrium surfaces, so it is not clear how well they would perform at large, time-dependent voltages, since there are no rigorous error bounds. For example, the double-layer differential capacitance in modified PB theories often increases with voltage [138], sometimes even faster than in PB theory [38], but we will argue below that it must decrease at large voltages, especially in concentrated solutions. In light of the scaling \(e\Psi_D/kT\) from PB theory (4.3), a related problem is that, until recently [148, 17], most theories have been unable to predict the decay of capacitance at low temperature in concentrated solutions. Although liquid-state theories for large voltages should certainly be developed, we will focus on much simpler mean-field, continuum descriptions of steric effects, in the hope of at least capturing some qualitative features of nonlinear dynamics analytically, across a large range of applied voltages.

Consistent with this approach, we will also work with the mean-field continuum description of electrostatic interactions (4.2), which neglects discrete many-body correlations. In passing, we point the reader to some of the extensive literature on corrections to PB electrostatics, for
the simplest possible model of an equilibrium liquid of point-like charges in a uniform dielectric medium. In the absence of specific interactions (such as steric repulsion), the fundamental length scale for ion-ion correlations is the Bjerrum length \( l_B = \frac{\varepsilon^2}{4\pi\varepsilon kT} \) at which the bare Coulomb energy balances the thermal energy. Interesting consequences of many-body electrostatics, not present in the mean-field PB description, include Oosawa-Manning condensation of counterions around charged rods in polyelectrolytes [137, 136, 120], renormalized charge of colloidal spheres [2, 15, 16], enhanced counterion localization around discrete surface charges [82], and counterion-mediated attraction of like-charged objects [78, 122, 79]. The latter phenomenon is believed to be responsible for the condensation of DNA in multivalent electrolytes [22], as well as the adhesion of cement plaste [78, 93]. A key part of the physics is the attraction between an ion and its “correlation hole” resulting from a fluctuation, which has recently been incorporated into a modified PB equation for a flat wall [163]. In all of these problems, however, the equilibrium surface charge is typically small (up to a monolayer of ions); it would be interesting to study electrostatic correlations at a much more highly charged surface, such as an electrode applying a large voltage, \( V \gg \psi T \) (our focus here).

Finally, we mention solvent effects, which are much less studied, and surely also very important at large voltages. Electrochemists widely believe that water dipoles in the Stern layer are so highly aligned by large electric fields that the effective permittivity drops by an order of magnitude (e.g. from 80\( \varepsilon_0 \) to 5\( \varepsilon_0 \)) [23]. At large applied voltages, where typical fields are of order \( V/\text{nm} \), it is reasonable to expect that the reduced permittivity would extend into the diffuse layer. This could have a major effect on ion-ion correlations, since the Bjerrum length \( l_B \propto \varepsilon^{-1} \) could get as large as 10 nm. Other aspects of water structure, such as hydrogen bonded networks, could also be altered by large electric fields and large ion concentrations. It would be interesting to perform \textit{ab initio} quantum-mechanical simulations of highly charged double layers to investigate such effects, beyond the primitive model.

4.1.4 Scope of the present work

In spite of the considerable literature on MPB descriptions of electrolytes in equilibrium or in steady state conduction, we are not aware of any attempt to go beyond dilute solution theory (PNP equations) in analyzing the dynamics of electrolytes in response to time-dependent perturbations, such as AC voltages. Accordingly, here we develop only some very simple models with the goal of identifying generic new features of diffuse-charge dynamics in a concentrated solution. As such, it is preferable to start with equations that capture the essential physics, while remaining analytically tractable, at least in some representative cases. For this reason, we focus on mean-field theories of steric effects and specifically build on the MPB equation of Bikerman [21] and Freise [60], which can be integrated analytically in a few simple geometries [29, 30, 28]. Such models also make reasonable predictions across the entire range of voltages.

The contribution is broken into two parts. Here, in chapter 4, we consider the canonical problem of charging a thin double layer, viewed as an effective circuit element [13]. We begin in section 4.2 by describing two simple models for steric effects in a quasi-equilibrium diffuse layer: (i) A “composite layer” model, consisting of a dilute PB outer region and, at high
voltage, an inner "condensed layer" of ions packed at the steric limit, and (ii) the Bikerman-Freise MPB model, which describes the same transition in a continuous fashion. In section 4.3, we then analyze the diffuse-layer capacitance and its role in equivalent circuit approximations. In section 4.4, we calculate steric effects on salt adsorption and tangential surface conduction by the diffuse layer, and discuss how these high-voltage effects affect and modify the applicability of circuit models. In section 4.5, we also briefly discuss the effects of a compact dielectric layer (which could model a Stern layer of adsorbed ions, or, more accurately, a thin film coating the solid), before concluding in section 4.6.

In the next chapter, we consider explicitly time-dependent problems with a general formalism, not only applicable to thin double layers. We start with the free energy functional of Borukhov et al.[29] and derive modified Poisson-Nernst-Planck equations (MPNP), based on a simple generalization of chemical potential (4.1) for concentrated solutions. As an illustration, we then repeat the nonlinear asymptotic analysis of Ref. [13] for the response of a blocking electrochemical cell (no reactions at the electrodes) to a suddenly applied voltage, to expose some general consequences of steric effects at large voltage. We also clarify the range of validity of the thin-double-layer circuit approximations derived here in this chapter.

### 4.2 Two models of steric effects in a thin diffuse layer

We focus on the response of a thin diffuse layer to an applied voltage, where it suffices to consider only quasi-equilibrium properties [13], as we justify carefully in chapter 5. Following Gouy and Chapman, we consider the case of a symmetric $z : z$ electrolyte here, although our reasoning is readily extendible to the general case. We also assume that the permittivity $\varepsilon$ is constant in space, which is certainly not correct when dense layers of ions form close to the surface. However, this can be taken into account in a following step and does not change the qualitative picture emerging from the following analysis. We will return to this point below in section 4.5.

There are at least three important lengths in our models. The first is the Debye length $\lambda_D$ given by (4.5), which sets the width of the diffuse layer at low voltage and low bulk concentration, $c_0$. The second is the mean spacing of ions in the bulk electrolyte, $l_0 = (2c_0)^{-1/3}$, and the third is the mean spacing of ions (essentially of the same sign) at the maximum concentration, $a = c_{\text{max}}^{-1/3}$. A fourth scale $L$ would characterize the geometry, as in chapter 5, but here we consider the regime of thin double layers, where $\lambda_D \ll L$. A fifth scale would be the Bjerrum length $l_B$, which we neglect by making the usual mean-field approximation.

From the first three lengths, there are two dimensionless groups. The first is $a/\lambda_D$, which we assume to be small for simple electrolytes in somewhat dilute solutions, so that steric effects are important only very close to the surface, at the inner portion of the diffuse layer (and even then, only at large voltages). The second dimensionless group can be written as the mean volume fraction of ions in the bulk,

$$\nu = 2a^3c_0 = (a/l_0)^3,$$

(4.11)
a natural measure of non-diluteness, which controls the importance of steric effects, along with the dimensionless voltage, $ze\Psi_D/kT$. In the figures below, we display results for $\nu = 0.00005, 0.005,$ and $0.5$ to span the range from dilute to highly concentrated solutions.
Figure 4-1: The dependence of the dimensionless parameter $\nu$ as a function of the bulk concentration $c_0$ and effective ion size $a$.

We stress that the phenomenological parameter $a$ is not necessarily the diameter of an ion, $a_0 \approx 1 \text{Å}$. We prefer to think of it as a cutoff for the unphysical divergences of PB theory, which we know must exist, and our goal is to understand its consequences. This cutoff length could include at least a solvation shell, e.g. $a \approx 3 \text{Å}$, but ion-ion correlations could effectively increase it further, since the Bjerrum length is at least $7 \text{Å}$. As noted above, taking into account the decrease of permittivity (by as much as a factor of ten) or other solvent effects at large fields could make $l_b$ and thus perhaps also $a$, as large as 10 nm. As a guide to using our results, we refer to Fig. 4-1 for the value of the dimensionless parameter $\nu$ for different values of $a$ and $c_0$.

4.2.1 A composite diffuse-layer model

In this model, we assume that the concentration fields are governed by Boltzmann distributions

$$c_\pm = c_0 e^{\pm ze\psi/kT}$$

(4.12)

wherever they are meaningful, that is, whenever these concentrations are weaker than a physical limit $1/a^3$, which is set by the ion size. For both ion species, if the formula (4.12) yields a quantity bigger than $1/a^3$, we set the concentration field of the counter-ion to be $1/a^3$, and assume that the coions are excluded from the corresponding condensed layer. The basic physics is shown in Fig. 4-2.

For most geometries, such as rough surface, this model is ill-posed and would require additional constraints to determine the location the sharp free boundary separating the "dilute" Boltzmann region and the "condensed" region at the maximum density. For a flat, semi-infinite diffuse layer with a given total charge $q_D$ or total voltage $\Psi_D$, however, the transition occurs at a single well defined position, $x = l_c$, away from the solid surface (at $x = 0$). In that case,
Figure 4-2: (a) Most prior work in electrokinetics has dealt with surfaces of pre-existing equilibrium charge at the scale of one electron per surface atom or less. This charge can be screened by roughly a monolayer of ions (partly in the diffuse layer) which corresponds to a "small" double layer voltage, of order $\psi_T = kT/e$. (b) In contrast, nonlinear electrokinetics deals with polarizable (mainly metal) surfaces, where much higher surface charge densities can be produced by an applied voltage or electric field nearby, and thus the double layer can "overcharge" to the point where dilute-solution theory no longer applies. The existence of a minimum ion spacing implies the formation of a condensed layer of counterions near the surface.

\[ c_{\pm} = c_0 e^{\pm ze\psi/kT} \] if $a^3 c_0 < 1$, $x > l_c$
\[ c_{\pm} = a^{-3}, c_\mp = 0 \] if $a^3 c_0 e^{\pm ze\psi/kT} \geq 1, 0 < x < l_c$  

(4.13)

Note that in this simplistic dichotomy the concentration field for co-ions is slightly discontinuous at the critical potential mentioned earlier,

\[ \Psi_c = \frac{kT}{ze} \ln \frac{2}{\nu} \]  

(4.14)

where again $\nu = 2a^3c_0$ is volume fraction occupied by (all) ions at zero potential in the bulk. Although very simple, this model already captures steric effects at large voltages to a great extent.

Let us compute the thickness $l_c$ of the corresponding layer of "condensed" counter-ions. We consider an electrode to which a strong negative potential $\Psi_D$ is applied to the diffuse layer.
with respect to the bulk, such that $|\Psi_D| = -\Psi_D > \Psi_c$ which leads to a condensed layer of positive ions in its vicinity.

Poisson’s equation for the thin diffuse layer reads

$$\varepsilon \frac{d^2 \psi}{dx^2} = -\rho$$

(4.15)

since (for now) the permittivity $\varepsilon$ is assumed constant. Within the condensed layer, we have $\rho = zec_+ = ze/a^3$, so by integrating, we obtain

$$\frac{d\psi}{dx} = -\frac{ze}{\varepsilon a^3}x + \frac{q_{cl}}{\varepsilon}, \quad \psi = -\frac{1}{2} \frac{ze}{\varepsilon a^3}x^2 + \frac{q_{cl}}{\varepsilon}x$$

(4.16)

where $-q_{cl}$ is the surface charge density on the electrode, so that $q_{cl}$ is the total charge per unit area in the diffuse layer.

Within the outer diffuse layer, the standard PB equation holds,

$$\varepsilon \frac{d^2 \psi}{dx^2} = 2zec_0 \sinh\left(\frac{ze\psi}{kT}\right)$$

(4.17)

which gives

$$\frac{d\psi}{dx} = -2 \sqrt{2kTc_0} \sinh\left(\frac{ze\psi}{2kT}\right)$$

(4.18)

At the interface between the condensed layer and the diffuse layer, we require the continuity of the electric field,

$$q_{cl} = 2zec_0 \lambda_D \left(\sqrt{\frac{2}{\nu}} - \sqrt{\frac{2}{\nu}}\right) + \frac{ze}{a^3}l_c$$

(4.19)

and of the electrostatic potential, so that

$$-\Psi_c = -\frac{kT}{ze} \ln(2/\nu) = -|\Psi_D| - \frac{1}{2} \frac{ze}{\varepsilon a^3}l_c^2 + \frac{q_{cl}l_c}{\varepsilon}$$

(4.20)

Combining these equations and solving for $l_c$ yields

$$l_c = \lambda_D \sqrt{2\nu} \left\{-1 + \nu \frac{\nu}{2} + \sqrt{1 - \nu^2 + \frac{ze|\Psi_D|}{kT} - \ln(2/\nu)}\right\}$$

(4.21)

which is plotted in Fig. 4-3 for several values of $\nu$. Generally, the condensed layer forms when the diffuse layer voltage $\Psi_D$ becomes only a few times the thermal voltage $kT/ze$, and then it grows sublinearly, proportionally to the square root of the potential drop as anticipated from Poisson’s equation with a constant charge density.

From this equation and (4.19), we finally obtain the charge/potential relation for the composite diffuse layer:

$$q_{cl} = 2zec_0 \lambda_D \sqrt{\frac{2}{\nu}} \sqrt{1 - \frac{\nu^2}{2} + \frac{ze|\Psi_D|}{kT} - \ln(2/\nu)}$$

(4.22)
which holds for $|\Psi_D| > \Psi_c$, as assumed here. For weaker potentials, there is no condensed layer and the standard PB model holds:

$$q_{pb} = -4z\varepsilon\varepsilon_0 \lambda_D \sinh \left( \frac{ze\Psi_D}{2kT} \right)$$

We note that, when compared to the PB charge density $q_{pb}$, the composite-layer charge density $q_{cl}$ is significantly reduced by the steric effects at higher $\Psi_D$. In particular, it increases only sublinearly, as opposed to exponentially in the PB model.

### 4.2.2 The modified PB model

The second model we consider is the classical mean-field description of steric effects in equilibrium mentioned in the introduction; a simple derivation can be found in the appendix B. We refer the reader to the literature for its various derivations and statistical mechanical assumptions [194, 60, 55, 90, 103, 26, 25, 29, 29, 30, 28]. For a symmetric $z:z$ electrolyte, the concentrations in the diffuse layer as a function of the electrostatic potential with respect to the bulk $\psi$ are given by the modified Boltzmann distribution

$$c_{\pm} = \frac{c_0 e^{\mp ze\psi/kT}}{1 + 2\nu \sinh^2 \left( \frac{ze\psi}{2kT} \right)}$$

where the packing parameter $\nu = 2a^3c_0$ is again the bulk ion density scaled to its maximum value and $a$ is the effective size of the ions and the solvent molecules. Note that the concentration
of each ion saturates and cannot exceed the steric limit\textsuperscript{1}.

In a mean-field approximation with these ion concentrations, the potential satisfies the modified Poisson-Boltzmann (MPB) equation,

\[ \nabla^2 \psi = \frac{z e \epsilon_0}{\epsilon} \frac{2 \sinh \left( \frac{z e \psi}{kT} \right)}{1 + 2 \nu \sinh^2 \left( \frac{z e \psi}{2kT} \right)}. \] (4.25)

Unlike the composite layer model, the MPB model can be applied to any geometry (just like the PB model). In the case of a flat diffuse layer, it gives a similar description, except that steric effects enter smoothly with increasing voltage, and there is no sharply defined condensed layer.

As for the first model, we can integrate the MPB equation across a thin double layer to obtain the normal electric field at the inner part of the diffuse layer

\[ \frac{d\psi}{dx} = -\text{sgn}(\psi) \frac{2 z e \epsilon_0 \lambda_D}{\epsilon} \frac{2}{\nu} \ln \left[ 1 + 2 \nu \sinh^2 \left( \frac{z e \psi}{2kT} \right) \right]. \] (4.26)

Integrating (4.15) using (4.26), we obtain for this model the relation between the charge per unit area in the diffuse layer \( q_{\text{mpb}} \) and the potential drop across it, \( \Psi_D \):

\[ q_{\text{mpb}} = -\text{sgn}(\Psi_D) 2 z e \epsilon_0 \lambda_D \frac{2}{\nu} \ln \left[ 1 + 2 \nu \sinh^2 \left( \frac{z e \Psi_D}{2kT} \right) \right]. \] (4.27)

This formula is illustrated in Fig. 4-4, and compared to the analogous formula for the composite diffuse-layer model (4.22). Although the charge-voltage relation (4.27) was derived by Freise\textsuperscript{2} [60] in 1952, since then it has been forgotten, or at least not explicitly stated in most studies [90, 103, 26, 25, 29, 29, 30, 28], who focused on the MPB concentrations (4.13).

We note in passing that the asymptotic behaviour at large voltages is similar for the two models presented, and corresponds to a layer of essentially constant charge density, which results, according to Poisson’s equation, in a total charge proportional to the square root of the potential drop.

4.3 Equivalent circuit elements

4.3.1 A word on circuit models

As widely recognized in electrochemistry [171, 119, 68], it is often appropriate to describe the effect of the double layers on the dynamic properties of a system through effective resistances

\textsuperscript{1}This saturation of the ion distribution with increasing voltage is analogous to Fermi-Dirac statistics in quantum mechanics for fermions obeying the Pauli exclusion principle.

\textsuperscript{2}Similarly, Chapman was the first to explicitly write down the formula (4.23) for the total charge [40], even though Gouy had thoroughly analyzed the concentration and potential profiles in the "Gouy-Chapman model" a few years earlier [73].
and capacitances. The underlying assumption, is that the equilibration time of the double layer is fast compared to the dynamics of the global "circuit" considered, essentially because it is so thin that transport processes within the double layer are rapid. A mathematical justification, starting from the simple PNP equations, can be given in terms of an asymptotic analysis of the thin double layer limit [13].

Therefore, we anticipate that for the many situations where the double layer is thin compared to the system size, the dynamics can be understood to a significant extent using the equilibrium characteristics of the double layer. These then provide appropriate boundary conditions for the dynamic transport processes in the bulk.

In particular, the analysis presented in Ref. [13], shows that the capacitance, or more precisely the differential capacitance "C", of the double layer is a central quantity allowing the modeling of the system in terms of an "RC" circuit. The second quantity of relevance, as it characterizes the entrance into the strongly non-linear regime, is the neutral salt uptake by the double layer which can result in an appreciable depletion of the bulk, leading to modifications of its conductivity (affecting the resistance "R" in the circuit) and thus of the dynamics. This paper and a subsequent one [45] also pointed out (in the context of dilute solution theory) that the tangential conduction through the diffuse layer is intimately tied to neutral salt adsorption, and indeed is governed by the same dimensionless "Dukhin number".

Therefore, we will proceed to compute all of these dynamical quantities for a thin quasi-equilibrium double layer, focusing on the general consequences of steric effects, which are common to the two models. After that, we will return to the question of surface capacitance and consider the effect of a thin dielectric layer (such as an oxide coating on a metal electrode, or perhaps a frozen Stern layer of adsorbed ions) on the overall dynamical response of the double layer.

Figure 4-4: The diffuse layer charge given by PB, MPB and CDL models as a function of the across potential drop.
4.3.2 Total and differential capacitances

The total capacitance of the diffuse layer can be obtained directly from the previous equations relating \( q \) (the charge per unit area in the diffuse layer) to \( \Psi_D \) (the voltage drop across the double layer), as simply \( -q(\Psi_D)/\Psi_D \). We have already computed these quantities above, and they are compared to the PB result (\( \nu = 0 \)) in Fig. 4-5. It is immediately obvious that the capacitance is greatly reduced at high voltage, compared to the predictions of dilute solution theory. The effect is so dramatic that the capacitance in both models reaches a maximum not much larger than the zero-voltage value, and even decreases for all values of voltage at sufficiently high concentration – the opposite trend from PB theory.

As noted above, the differential capacitance, defined for the diffuse layer as

\[
C_D(\Psi_D) = -\frac{dq}{d\Psi_D}
\]  

is the relevant quantity for the dynamical response to an applied voltage. Throughout this chapter, to be clear, we will use the notation \( C \) only for the differential capacitance. In the PB model (\( \nu = 0 \)), the differential capacitance from Eq. (4.23) has already been noted above:

\[
C_D^\nu = \frac{\epsilon}{\lambda_D} \cosh \left( \frac{ze\Psi_D}{2kT} \right).
\]  

For the composite diffuse layer (CDL) model introduced above, (4.19) yields

\[
C_D^\nu = \frac{\epsilon}{\lambda_D} \frac{1}{\sqrt{2\nu \sqrt{(1 - \nu^2)^2 + \left(\frac{ze|\Psi_D|}{kT} - \ln(2/\nu)\right)}}}
\]
when $\Psi_D > \Psi_c$. Otherwise, the PB formula (4.29) still holds. For the MPB diffuse layer model, using (4.27), we find

$$C_D^\nu = \frac{\frac{\varepsilon}{\chi_D} |\sinh(\frac{e\psi}{kT}\rho)|}{[1 + 2\nu \sin^2 \left(\frac{e\psi}{2kT}\right)]^{\frac{3}{2}} \ln[1 + 2\nu \sin^2 \left(\frac{e\psi}{2kT}\right)]} \quad (4.31)$$

The different models are compared in Fig. 4-6.

The qualitative trends in $C$ are again similar in both models of steric effects and dramatically different from PB theory. For both models, the differential capacitance increases at very low potentials (comparable to the thermal voltage, $kT/ze$) as it does in the PB model because steric effects are still negligible. These enter the picture at larger potentials and limit the storing capacity of the layer, with a differential capacitance that actually decreases to zero at large potentials. As a consequence both models predict a non-monotonic differential capacitance, and show a maximum at intermediate values.

Of course, there are some clear differences in the detailed predictions of the two models, shown in Figs. 4-6. Although the limiting behaviors at large and small voltage are similar, the transition is unphysically sudden in the CDL model, compared to the more reasonable, smooth transition in the MPB model. This is especially true at low concentrations, where the sudden, delayed appearance of steric effects in the CDL model gives rise to a sharp cusp in the differential capacitance versus voltage. At high concentrations, where the “low voltage” regime of dilute solution theory effectively vanishes, the CDL model also fails to predict the immediate onset of steric effects, even at small voltages, which causes a monotonic decrease in differential capacitance – the opposite trend of the PB model. Nevertheless, the CDL model manages to approximate the trends of the MPB model well, with an appealingly simple physical picture.

In summary, three basic features show up in both models, which we take as an indication...
that they qualitatively hold irrespective of the specific approximations embedded in each model: (i) the differential capacitance \( C_D(\Psi_D) \) is weaker at moderate and high potentials than if steric effects are neglected (as in the PB scheme); (ii) at moderate concentrations, the differential capacitance varies non-monotonously with a peak at intermediate voltages and a slow decrease towards zero at higher voltages, (iii) at the steric limit \( (\nu = 1) \), the differential capacitance is a strictly decreasing function of voltage (in the MPB model). These effects are all explained by the strong tendency of ions to form a condensed inner layer at high voltage and/or high concentration, when steric effects are taken into account. This greatly reduces the differential (and total) capacitance compared to classical PB theory, which neglects the finite size of ions, and thus predicts an absurd exponential pile-up of ions extremely close to the surface (less than one molecular radius) in the nonlinear regime.

4.3.3 Diffuse-layer charging dynamics

These revelations have important consequences for our understanding of double-layer charging in many situations. In the simplest picture of an equivalent RC circuit, with \( R \) the resistance of the bulk, these statements relate to the response time of the system to a step or an AC applied voltage. The typical response time for a driving of amplitude \( V \) is \( \tau_c(V) = R C_D(V) \), so the classical picture from PB theory (4.29) has been that nonlinearity greatly slows down the charging dynamics [118, 169, 13, 45, 177, 135]. Although this may occur in a dilute solution for a relatively small range of voltages (typically only several times the thermal voltage), steric effects in a concentrated solution bound the relaxation time at a value much less than expected from the PB model, in both the CDL and MPB models. This is clear in Fig. 4-7, where we solve the RC circuit dynamics

\[
C_D(\Psi_D) \frac{d\Psi_D}{dt} = \frac{V - \Psi_D}{R}
\]

for the three models numerically, to obtain the diffuse-layer voltage \( \Psi_D(t) \) in response to a suddenly applied voltage \( V \) across the layer in series with a bulk resistance \( R \). In addition, importantly, the response time of an electrolytic cell is found to decrease with the amplitude of the applied voltage above the threshold for strong steric effects, \( V > \Psi_c \). As shown in Fig.4-7(b), the relaxation is faster for \( V = 20kT/ze \) than for \( 10kT/ze \), since \( \Psi_c = 8.3kT/ze \) for \( \nu = 0.005 \).

4.4 Beyond circuit models

4.4.1 Diffuse layer salt adsorption

As recently pointed out in Ref. [13], circuit models can break down at large voltages if a large number of ions (mostly counter-ions) are engulfed by the diffuse layers with a resulting depletion of ions in the bulk. The total salt concentration in the diffuse layer (counter-ions plus co-ions) increases with voltage, regardless of the sign of the charge. Therefore, a diffusion layer forms and relaxes into the neutral bulk whenever a voltage is applied across a double layer at a blocking surface (although reactions and/or rejection of adsorbed ions from the Stern layer could lead to negative adsorption or salt expulsion in other situations [116]). In the absence of salt injection by the surface, the positive adsorption of neutral salt by the diffuse layer is present in the PB
description, where the counter-ion concentrations increase exponentially with voltage [13]. It is still present but obviously weaker in models accounting for steric effects, which severely limit the capacitance of the diffuse layer to store additional ions at high voltage. We now quantify this statement using the two simple models introduced above.

Following notations introduced in Ref. [13], we define the excess neutral salt in the double layer as

\[
w = w' = \int_{\text{surface}}^{\text{bulk}} (c_+ + c_- - 2c_0) dx.
\]

For the PB model one finds [13],

\[
w^{\nu = 0} = 8c_0\lambda D \sinh^2 \left( \frac{z e \Psi D}{4 kT} \right).
\]  

(4.33)

For the CDL model, the same equation holds for \( \Psi_D < \Psi_c \), while above this value \( \Psi_D > \Psi_c \) we obtain

\[
w^{\nu} = \left( \frac{2}{\nu} - 2 \right) c_0 l_c + 2c_0\lambda D \left( \sqrt{\frac{2}{\nu}} + \sqrt{\frac{2}{\nu} - 2} \right)
\]  

(4.34)
Figure 4-8: The diffuse layer neutral salt uptake \( w \) as a function of the potential difference \( \Psi_D \).

with \( l_c(\Psi_D) \) to be extracted from (4.21). For the MPB model

\[
\nu' = \int_0^{\Psi_D} \frac{2e\lambda_D (1 - \nu) du}{\sqrt{2} \ln (1 + 2 \nu \sinh^2 u)}
\]

which we can compute numerically.

Unlike the PB formula (4.33), which predicts exponentially diverging salt uptake for increasing \( \Psi_D \), the steric modified formulae (4.34) and (4.35) predict sublinear (square-root like) dependence on \( \Psi_D \), at large voltages, as can be seen by inspection of (4.33)-(4.35) or from the plots in Fig. 4-8. This can be understood qualitatively as a consequence of the roughly square-root voltage dependence of the condensed layer width (due to its constant charge density), since most of the adsorbed ions are condensed counterions at large voltages. (See Fig. 4-3 and Eq. (4.21) for the CDL model.) Another way to see it in both models is that the total salt adsorption is asymptotic to the total charge, \( w \sim q/ze \), which is true for any nonlinear double layer model (PB, MPB, CDL,...) since the coion density goes to zero across most of the diffuse layer at large voltages. As explained in Ref. [13], in response to an applied voltage the neutral bulk electrolyte becomes depleted, as the electric field draws counterions into the diffuse layer and conducts coions away through the bulk, resulting in a slowly expanding diffusion layer, reducing the bulk concentration accordingly.

The main feature, again common to both models, is that the salt uptake at large voltage is greatly reduced in comparison to the exponential growth predicted by the PB picture. This is important for the dynamics as this quantity sets the limit of applicability of the widely used RC circuit model [13]. This equivalent circuit approximation should thus hold up to much larger values of potential when steric effects are included.
4.4.2 Breakdown of circuit models

With analytical expressions for total salt adsorption by the diffuse layer, we can estimate the upper limits on the applied voltage where the circuit approximation breaks down in the various models. For an electrolyte cell of thickness $2L$, the salt uptake by the diffuse layer corresponds to a removal of $2w$ charge carriers (ions) per unit surface, from a bulk that contained $2c_0L$ such carriers initially. As long as the ratio of these two quantities $w/(c_0L)$ is small, the total resistance of the RC circuit is roughly unaffected by the salt adsorption. So, an estimate for the limit is [13]

$$\alpha_s = \frac{w}{c_0L} \ll 1,$$

which translates an upper bound on the applied voltage, $|V| < V_{\text{threshold}}$ for the RC description to remain valid (in the thin double layer limit $\lambda_D/L \ll 1$). For the PB model, the upper bound,

$$V_{\text{threshold}} \approx \frac{2k_BT}{Ze} \ln \left( \frac{L}{4\lambda_D} \right) \quad \text{(dilute)},$$

is not much larger than the thermal voltage, due to the weak logarithmic dependence on $L/\lambda_D$.

For the models accounting for steric effects, however, the upper bound is greatly increased in concentrated solutions,

$$V_{\text{threshold}} \approx \frac{k_BT}{Ze} \left( \frac{L}{\lambda_D} \right)^2 a^3 c_0 \quad \text{(non-dilute)}.$$

This shows that the widely used circuit approximation for a thin double layer $\lambda_D \ll L$ does not break down until enormous voltages, $V \propto (L/\lambda_D)^2$, in a concentrated solution. In a very dilute solution, where $\nu = 2a^3c_0 \ll 1$, the circuit approximation may break down at moderate voltages, but only in a microsystem, where the double layers are not so thin. For example, even in an (aqueous) electrolyte with $\lambda_D = 10$ nm, $c_0 = 10^{-3}$ M, $a = 5\text{Å}$ and in a microdevice with $L = 100\mu\text{m}$ features, the threshold voltage (with steric effects) is roughly 0.2 Volts.

This estimate, however, neglects the possibility of a transient breakdown of the RC circuit approximation, prior to diffusive relaxation across the entire cell. In the case of response to a suddenly applied DC voltage, the salt adsorption by each the diffuse layer occurs over a time scale, $\tau_c = \lambda_D L / D$, during which diffusion spreads the nearby region of depleted neutral bulk solution over a distance $\sqrt{D\tau_c} = \sqrt{\lambda_D L}$. Therefore, the requirement that the local bulk conductivity does not change significantly during charging dynamics yields the refined estimate [13],

$$\alpha_d = \frac{w}{c_0\sqrt{\lambda_D L}} \ll 1$$

which replaces $L/\lambda_D$ by $\sqrt{L/\lambda}$ in the estimates above. This sets a lower bound for the limiting voltage for the validity of circuit models.

In the case of AC forcing at frequency $\omega$, the bound $\alpha_d \ll 1$ is appropriate for low frequencies, $2\pi\omega\tau_c \ll 1$, but circuit models remain valid up to higher voltages at higher frequencies. At moderate frequencies, $2\pi\omega\tau_c > 1$, the double layer does not have enough time for complete charging, and the Warburg-like diffusion layer due to salt adsorption (which oscillates at twice the frequency) only propagates to a distance, $\sqrt{D/4\pi\omega}$. Therefore, we may crudely estimate
\[(w/c_0)\sqrt{4\pi \omega D} \ll 1\] to avoid significant changes in bulk conductivity in the diffusion layer. (A more careful estimate would take into account that only partial charging and salt adsorption occur with increasing frequency.) At higher frequencies, \(\omega \lambda^2 D / D \approx 1\), the diffuse layer does not have enough time to equilibrate, and little charging occurs.

These arguments can be made more precise using matched asymptotic expansions to describe the thin double layer limit, starting from an explicitly time-dependent model. For the case of one-dimensional response to a suddenly applied voltage, this was done in Ref. [13] starting from the Poisson-Nernst-Planck equations of (time-dependent) dilute solution theory. In chapter 5, we will derive modified PNP equations for dynamics with steric effects and repeat the same kind of asymptotic analysis to reach a similar conclusion our simple arguments here: Steric effects greatly extend the range of applicability of RC circuit models, compared to what would be expected on the basis of dilute solution theory.

4.4.3 Diffuse-layer surface conduction

Another feature not present in circuit models is the possibility of current passed along the surface through the diffuse layer, demonstrated by Bikerman [19] and considered extensively in theories of electrokinetics by Dukhin and collaborators [52]. As first shown in Ref. [13] and elaborated in Ref. [45] in the setting of dilute solution theory, the relative strengths of tangential “surface fluxes” through the diffuse layer, compared to bulk fluxes, are controlled by the same dimensionless groups that govern ion adsorption (discussed above). This is actually quite a general result, as we now briefly explain. We will thus conclude that steric effects also greatly reduce the importance of surface conduction in the diffuse layer compared to the classical predictions of dilute solution theory.

Assuming small local perturbations from thermal equilibrium, the flux density (number/area·time) of ionic species \(i\) is given by

\[F_i = -b_i c_i \nabla \mu_i \tag{4.37}\]

where the chemical potential \(\mu_i\) generally has a different form than (4.1) in a concentrated solution (e.g. see chapter 5). Consider a thin diffuse layer near a charged surface, where the ion concentration \(c_i\) departs from its nearby neutral bulk value \(c_i^b\). Due to fast relaxation at the small scale of the screening length, the diffuse-layer concentration remains in quasi-equilibrium at nearly constant chemical potential in the normal direction, \(\mu_i \sim \mu_i^b\), in the thin double layer limit. There can, however, be small tangential gradients, \(\nabla \parallel \mu_i \neq 0\) at the macroscopic length scale leading to an excess diffuse-layer “surface” flux density (number/length·time):

\[F_i^s = \int_{\text{surface}}^{\text{bulk}} (-b_i c_i \nabla \parallel \mu_i + b_i c_i^b \nabla \parallel \mu_i^b) \, dx \tag{4.38}\]

\[\sim -\nabla \parallel \mu_i^b \int_{\text{surface}}^{\text{bulk}} b_i (c_i - c_i^b) \, dx. \tag{4.39}\]

For a constant mobility \(b_i\), this takes the same form as the bulk flux density (4.37),

\[F_i^s = -b_i \Gamma_i \nabla \parallel \mu_i \tag{4.40}\]

where the bulk concentration (number/volume) has been replaced by the diffuse-layer “surface
concentration” (number/area),

\[ \Gamma_i = \int_{\text{surface}}^{\text{bulk}} (c_i - c_i^b) \, dx \]  

(4.41)

In a concentrated solution, we generally expect that the mobility \( b_i \) might decrease in the diffuse layer, due to steric effects and large normal electric fields, so this formula may overestimate the surface flux density.

Following Bikerman [19, 20, 45], we may estimate the relative importance of surface to bulk flux densities at a length scale \( L \) by the dimensionless group

\[ \frac{F_i^s}{F_i^b L} = \frac{\Gamma_i}{c_i^b L} \]  

(4.42)

which we see also measures the relative importance of “surface adsorption” of ion \( i \) in the diffuse layer relative to the bulk concentration. For a highly charged diffuse layer \(|\Psi_D| \gg \Psi_c\), the ions are mostly of one type (counter-ions), so \( \Gamma_i \sim q \sim w \). The surface current is also carried mostly by those ions, \( J^s \sim zeF_i^s \), while the bulk current is carried by both ions, \( J^b \approx 2(ze)F_i^b \) (neglecting diffusion compared to electromigration). Therefore, we see that the “Dukhin number” comparing surface conduction at a highly charged diffuse layer to bulk conduction at nearly uniform concentration,

\[ Du = \frac{J^s}{J^b L} \sim \frac{w}{2c_0 L} = \frac{\alpha_s}{2} \]  

(4.43)

is roughly half of the dimensionless group \( \alpha_s \) governing salt adsorption by the diffuse layer.

We have seen that steric effects greatly reduce \( w \) compared to the predictions of dilute solution theory, so that \( \alpha_s = O(\lambda_D / L) \) remains small up to rather high voltages. Since the calculation above over-estimates the importance of surface conduction, it is clear that steric effects also greatly reduce the Dukhin number compared to the predictions of dilute solution theory. We conclude that surface conduction in a thin diffuse layer does not become important until voltages large enough to violate the equivalent circuit approximation are applied across it. Compact layer surface conduction may still be important in some cases, but it too is limited by the same steric effects.

### 4.5 Compact Layer Effects

We now check the robustness of these conclusions to the additional presence of an insulating surface layer between the metal electrode and the electrolyte where the EDL models are applied. We suppose that this layer is not involved in the dynamics so that its properties do not change, and assume for the sake of simplicity that these properties are linear so that it can be described as a fixed surface capacitance \( C_s \).

Such models have been used in many circumstances, sometimes to describe the Stern layer corresponding to condensed ions. Our approach here is different in the sense that a layer of condensed ions would be involved in the charging/discharging process. What we have in mind is closer to a thin film, e.g. of oxide on the metal, of thickness \( h_s \) and dielectric constant \( \epsilon_s \).
so that $C_s = \varepsilon_s/h_s$. This form has been proposed to model coating layers on electrodes in the context of AC electrokinetics [1].

The overall differential capacitance of the interface is now

$$\frac{1}{C} = \frac{1}{C_D} + \frac{1}{C_S}$$

with $C_S = dq/d\Psi_S$, where $q$ is the total charge per area in the double layer, and $\Psi_S$ is the voltage drop across the aforementioned compact layer. The total voltage drop across the interface is $\Psi = \Psi_S + \Psi_D$, and $q/\Psi$ is the total capacitance of the interface.

A useful dimensionless parameter to quantify the effect of this surface layer is $\delta = \varepsilon/(\lambda_D C_S)$, which has been employed recently in general studies of diffuse-charge dynamics [27, 13], as well as in theoretical models [1, 72, 145, 12, 177, 135] and in the fitting of experimental data [108, 144] for induced-charge (AC or DC) electrokinetics. No surface layer corresponds to $\delta = 0$. In the above mentioned picture of the layer of oxide, $\delta = (\varepsilon/\varepsilon_s)(h_s/\lambda_D)$ so that even very thin oxide layers can yield not too small values of $\delta$ if $\varepsilon/\varepsilon_s$ is large.

Let us now compare the differential capacitance $C$ (with surface layer) to the bare double layer differential capacitance previously plotted in Fig.4-6, for the PB equation and the two models with steric effects. The corresponding plots are provided on Fig.4-9 for $\delta = 0.25$.

Many qualitative points are obvious. First, the PB differential capacitance does not blow up exponentially anymore, as the surface layer takes over when the double layer voltage gets large, so that $C$ converges to the finite value $C_s$ within the PB model. Most of the potential drop is then across the surface layer. Second, the two main consequences of steric effects pointed above remain valid: $C$ is weaker when steric effects are taken into account, and $C(\Psi)$
Figure 4-10: The differential capacitance $C$ of the double layer as a function of potential difference $\Psi$ for various values of Stern layer capacitance.

is nonmonotonous with a maximum at intermediate values and a further decrease to zero.

When the parameter $\delta$ is zero or small (i.e. the Stern layer capacitance is large), a closely packed "diffuse" layer has to form in response to a high potential drop. This is the case when the steric effects become important and the PB theory fails. However, for the higher values of $\delta$, most of the potential drop is realized over the Stern layer, and the ions in the diffuse layer are not as densely packed. Thus the system stays below the steric limit, and the PB theory agrees with the MPB theory, as demonstrated by the total capacitance plots of Fig. 4-10.

Similar comments can be made on Fig.4-9, which shows that for $\delta = 0.25$, steric effects may or may not be important depending on value of the dimensionless parameter $\nu = 2a^3c_0$. For the distribution of the voltage drop over the Stern layer and the diffuse layers, see Fig.4-11.

This analysis, although correct, is somewhat misleading, however, since the assumption of a constant compact-layer capacitance may not always be reasonable. In many situations of interest, where several volts ($\approx 100kT/e$) are applied across the double layer, it is unlikely that the compact layer could withstand a significant fraction of the total voltage. Note that dielectric breakdown in water can occur in average fields as low as 20 MV/m = 0.02 V/nm in experiments applying submicrosecond voltage pulses (well below the charging time of the double layers) [92]. The critical field may be higher in the Stern layer, where water is confined by ions at the outer Helmholtz plane [23], but it seems implausible for an atomic layer to sustain several volts without somehow "short circuiting" via electron cascades, electrolysis, Faradaic reactions, etc. In some cases, the compact layer models a dielectric thin film, which may be considerably thicker. Again, however, most coating materials, such as teflon or various metal oxides, undergo dielectric breakdown in fields of order 10 MV/m, so a dielectric coating cannot easily withstand several volts unless it is at least 10 nm wide.

In general, we see that the capacitance of the compact layer must effectively decrease at
Figure 4-11: The Stern layer voltage drop as a function of the total double layer voltage difference. For reference, the line $\Psi_s = \Psi$ is also drawn. In the PB theory, almost all of the voltage drop is realized over the Stern layer when the voltage drop is on the order of a few voltages.

large voltages, which corresponds to the limit $\delta \to 0$. As a result, a significant fraction of a large voltage must be sustained by the diffuse layer, making steric effects important in many situations of interest. Regardless of the accuracy of our simple models, therefore, we believe that the predicted qualitative effects of ion crowding are likely to have broad relevance for experimental systems applying large voltages.

4.6 Conclusion

We have used two simple models for the double layer to account for crowding effects which necessarily take place at intermediate and large applied voltages. These models are both based on modifications of the Poisson Boltzmann description of dilute solutions. This strategy has lead us to identify important operational consequences of these crowding effects the thin double layers, namely a largely reduced double layer capacitance and a decreased ion uptake from the bulk.

We have provided in these sections explicit formulas for the total and differential capacitance and for the salt uptake of interfaces at equilibrium, as a function of the potential drop across the interface. More precisely we have recalled the PB results (no steric effects $\nu = 0$), and given results for the two simple models with steric effects ($\nu \neq 0$), considering for all cases the possibility of a finite insulating layer on the electrode ($\delta \neq 0$).

The two models lead to remarkably similar results suggesting that these semi-quantitatively hold beyond the specifics of these models. Both showed marked differences with the PB approach: the differential capacitance and salt uptake are much weaker, and the former varies non-monotonously with the applied potential.
These observations for the equilibrium properties have led us to make predictions for the dynamics of electrolyte cells of size quite larger than the Debye length: (i) an effective equivalent RC circuit description holds for a wider range of potentials than expected on the simple basis of the PB equation, (ii) the response time is much smaller than expected from PB at large voltages, (iii) this time decreases at large voltages after an initial increase for lower values.

The dramatic effect of steric constraints in this problem also shows that other predictions of nonlinear PB theory, such as the change of scaling from $V^2$ to $|V|\log|V|$ for AC electro-osmosis [135], are limited in applicability and should be revisited with models taking crowding effects into account. More generally, this work suggests that, beyond the present problem of ionic transport in electrolytic systems, the description of electrokinetic effects at large applied voltages should be revisited to correct shortcomings of dilute-solution theory.
Chapter 5

Modified PNP Equations

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5.1 Introduction

In situations involving large potentials or surface charges, the Poisson Boltzman (PB) equation has shortcomings because it neglects ion-ion interactions and steric effects. This has been widely recognized by the electrochemistry community, leading to the development of various alternative models resulting in different sets of "modified PB equations", which have had at least qualitative success in predicting equilibrium ion distributions. On the other hand, the literature is scarce in terms of descriptions of concentration dynamics in these regimes. Here, adapting strategies developed to modify the PB equations, we propose a simple modification of the widely used Poisson-Nernst-Planck (PNP) equations for ionic transport, that at least qualitatively accounts for steric effects. We analyze numerical solutions of these MPNP equations on the model problem of the charging of a simple electrolyte cell, and compare the outcome to that of the standard PNP equations. Finally, we repeat the asymptotic analysis of [13] for this new system of equations to further document the interest and limits of validity of the simpler equivalent electrical circuit models introduced in chapter 4 for such problems.

In chapter 4, we focused on steric effects of finite ion size on the charging dynamics of a quasi-equilibrium electrical double layer, motivated by the breakdown of the classical Gouy-Chapman model [115] at large voltages (up to several Volts and $\gg kT/e = 25$ mV), e.g. which are commonly applied in AC electro-osmosis [146, 32, 183, 108, 189]. We introduced two simple modifications of the Boltzmann equilibrium distribution of ions to incorporate steric constraints. Both new models predicted similar dramatic consequences of steric effects at large voltages, such as greatly reduced diffuse-layer capacitance and neutral salt uptake from the bulk compared to the classical theory. The crucial effect of the finite ion size is to prevent the unphysical crowding of point-like ions near the surface at large voltages by forming a condensed layer of ions at the close-packing limit (likely to include at least a solvation shell around each ion).

The idea that the electric double layer acts like a capacitor is part of a bigger picture and suggests that the dynamics can be described in terms of equivalent circuits [119, 68], where the double layer remains in quasi-equilibrium with the neutral bulk. This classical
approximation has been discussed and validated in the thin double layer limit by asymptotic 
analysis of the Poisson-Nernst-Planck (PNP) equations [13]. The PNP equations provide the 
standard description of the linear-response dynamics of electrolytes perturbed from equilibrium, 
based on the same assumption of a dilute solution of point-like ions interacting through a mean 
field which underlies the PB equation for equilibrium [133, 115].

Here we try to account for the effect of steric constraints on the dynamics, by first establishing 
modified PNP (MPNP) equations using linear response theory and modified electrochemical 
potentials. We apply the MPNP equations to describe the charging of a parallel plate electrolyte 
cell in response to a suddenly applied voltage and comment on the differences with usual PNP 
dynamics. The results are in line with the work in chapter 4 since the double layer behaves 
like a capacitor; however its capacitance is reduced by steric effects, and neutral salt uptake is 
decreased as well.

Finally, following the analysis of Bazant, Thornton, and Ajdari [13], we demonstrate that the 
considerations of chapter 4 can rigorously be supported by asymptotic analysis on the MPNP 
equations. This helps us understand the limits of the electric double layer capacitor models 
and define rigorously what is meant by the thin double layer limit.

5.1.1 Electrolyte Dynamics in Dilute Solution Theory

As we have mentioned in chapter 4, the dilute solution theory has been the default model for ion 
transport for the most part of the twentieth century. According to this theory, it is acceptable 
to neglect interactions between individual ions. As a result, the electrochemical potential takes 
the form

$$\mu^\text{dilute} = kT \ln c_i + z_i e \psi$$

(5.1)

where $z_i e$ is the charge, $c_i$ the concentration, and $\psi$ the electrostatic potential-usually governed 
by the Poisson’s equation. In order to derive an equation for the electrolyte dynamics, we need 
to combine the above equation with the flux formula (here with the standard assumption that 
interactions between different species are negligible, see e.g. [7, 132, 160])

$$F_i = -b_i c_i \nabla \mu_i$$

(5.2)

(where $b_i$ is the mobility of the species $i$) and the general conservation law,

$$\frac{\partial c_i}{\partial t} = -\nabla \cdot F_i$$

(5.3)

The resulting equations,

$$\frac{\partial c_i}{\partial t} = \nabla \cdot \left( D_i \nabla c_i + b_i z_i e c_i \nabla \psi \right)$$

(5.4)

are called the Nernst-Planck (NP) equations. Here, the Einstein’s relation, $D_i = b_i / kT$, relates 
the ions mobility $b_i$ to its diffusivity $D_i$. The system is closed by the Poisson’s equation,

$$-\nabla \cdot (\varepsilon \nabla \psi) = \sum_i z_i e c_i$$

(5.5)

where $\varepsilon$ denotes the permittivity of the electrolyte. The name Poisson-Nernst-Planck (PNP) 
equations is coined for the system defined by equations (5.4) and (5.5). The standard PNP
system presented above has been used to model selectivity and ionic flux in biological ion channels [56, 124, 35, 83, 84], AC pumping of liquids over electrode arrays [146, 1, 72, 32, 145, 9], induced-charge electro-osmotic flows around metallic colloids [64, 126] and microstructures [177, 108, 9], dielectrophoresis [165, 170, 178] and induced-charge electrophoresis [12, 195, 178, 162] of polarizable particles in electrolytes.

As explained thoroughly in chapter 4, however, the dilute solution theory, including the PNP equations, has limited applicability: its predictions easily violate its basic assumption (i.e. being dilute) near surfaces of high potential. In fact, this happens more often than not due to the exponential (Boltzmann-type) dependence of counter-ion concentration on electrostatic potential. The steric limit, that is $c_{\text{max}} = 1/a^3$, $a$ being the typical spacing between densely packed ions, is reached at the critical potential

$$
\Psi_c = -\frac{kT}{ze} \ln(c_0a^3) = \frac{kT}{ze} \ln\left(\frac{c_{\text{max}}}{c_0}\right)
$$

where $c_0$ is the bulk electrolyte concentration of either of the species. Due to the logarithmic dependence in its formulation, the critical voltage $\Psi_c$ is no more than a few times the thermal voltage $\psi_T = kT/ze$ and therefore easily reached in many applications such as the induced charge electroosmosis [64, 126]. This has motivated researchers to modify the standard equations and improve the dilute solution theory (see next subsection).

### 5.1.2 Beyond Dilute Solution Theory

Statistical mechanics have proved to be an indispensable tool for analyzing and improving the dilute solution theory. In particular, a statistical model with the desired level of detail can be set up, and after the corresponding free energy $F$ is calculated, the chemical potentials can be obtained from the formula

$$
\mu_i = \frac{\delta F}{\delta c_i}
$$

where $c_i$ is the concentration of the $i$-th species. Then differential equations governing the electrolytes can easily be derived from this chemical potential as outlined in the previous subsection. There have been many attempts to calculate the free energy of the electrolyte more accurately to improve the dilute solution theory (see below for references). In some of these attempts, the calculation of the free energy was replaced by an equivalent consideration of mean electrostatic potential and mean charge density [106, 138, 38, 139, 140, 39]. Using those mean quantities, various correlation functions as well as new and more accurate PB (i.e. MPB) equations have been proposed. However, one should keep in mind that the corresponding free energies can still be calculated for these models, too.

Perhaps the first examination of the limits of the dilute solution theory by statistical mechanical considerations was by Kirkwood [101] in 1934. After a detailed analysis of the approximations of the dilute solution theory, Kirkwood concluded that those approximations consisted of the neglect of an exclusion-volume term and a fluctuation term. Furthermore, he gave estimates of those terms and argued that they are indeed negligible in the bulk electrolyte. In recent years, there have been many attempts [106, 138, 38, 139, 140, 39] originating from the liquid-state theory to calculate those neglected terms more explicitly, which resulted in a variety of MPB equations (including the MPB1,...,MPB5 hierarchy of Outhwaite and Bhuiyan [138]).
Another general approach to the statistical mechanics of electrolytes is based on density functional theory (DFT). Using this formalism, Rosenfeld [154, 155, 156] systematically derived elaborate free energy functionals for neutral and charged hard-sphere liquids starting from basic geometric considerations. Gillespie et al. [69, 70, 71] calculated chemical potentials from Rosenfeld’s free energy functionals, and used them along with the formula (5.2) to calculate the steady flux in an ion channel, as well as to investigate the equilibrium structure of the double layer. With this theoretical framework, Roth and Gillespie [157] were able to explain size selectivity of biological ion channels.

The DFT has also been used to investigate solvent effects, which become important at high voltages. Tang, Scriven and Davis [186, 198, 187] have developed a three component model (3CM) by considering the solvent molecules as neutral hard spheres in an attempt to investigate solvent exclusion effects. These authors have also analyzed the structure of the electrical double layer with their (3CM) approach, and were able to capture the non-monotonic behaviour of the differential capacitance. Indeed, their results look very similar to ours in chapter 4.

Perhaps one reason why neither the MPB hierarchy of Outhwaite and Bhuiyan [138], nor the free energy functionals of Rosenfeld [156], nor the (3CM) model of Tang et al. [198] has gained widespread use and recognition is their intrinsic complexity which limits their simple application to specific problems. For example, the hard sphere component of Rosenfeld’s free energy density is given by

$$\Phi_{HS} = -n_0 \ln (1 - n_3)$$

$$+ \frac{n_1 n_2 - n_{V1} n_{V2}}{1 - n_3} + \frac{n_2^3}{24\pi (1 - n_3)^2} \left(1 - \frac{n_1^2}{n_2^2}\right)^3$$

where each of $n_0, n_1, n_2, n_3, n_{V1}$, and $n_{V2}$ are functions defined in terms of (in general 3D) integrals. So the improvements over the initial PB equations are made at the cost of losing the possibility of analytical progress, and nontrivial numerical work is required even for simple problems in one dimension.

Because of their mentioned complexity, the application of the improvements to the dilute solution theory have mostly been restricted to analyzing the equilibrium properties of electrolytes, such as the structure of the electrical double layers. For a review on the subject, we refer the reader to references in chapter 4, e.g. [5].

A considerably simpler approach, which mainly focuses on the contribution of size effects to the free energy, is based on mean-field theory together with the lattice-gas approximation in statistical mechanics. Following the early work of Eigen and Wicke [194, 60, 55], Iglic and Kral-Iglic [90, 103, 26, 25] and Borukhov, Andelman, and Orland [29, 30, 28] were able to come up with a simple statistical mechanical treatment which captures basic size effects. A free energy functional is derived by mean-field approximations of the entropy of equal-sized ions and solvent molecules. This free energy is then minimized to obtain the equilibrium average concentration fields, and the corresponding modified PB (MPB) equation. While more complex than the original PB equation, it is still rather compact and simple, and definitely amenable to further analytical use.
5.1.3 Scope of the present work

All of the above authors, as well as others we have cited in chapter 4, focus on the equilibrium or steady state properties of the electrolytes. In fact, we are not aware of any attempt to go beyond the dilute solution theory (PNP equations) in analyzing the dynamics of electrolytes in response to time-dependent perturbations, such as AC voltages. Here in the second part of this series, our aim is to improve the (time-dependent) PNP equations of the dilute solution theory by incorporating the steric effects in a simple way with the goal of identifying new generic features. Our focus is electrolyte systems that contain highly charged surfaces, such as an electrode applying a large voltage \( V \gg \psi_T = kT/ze \), where the steric effects become important quantitatively as well as qualitatively. As in chapter 4, here we again adopt the mean-field approach of Iglic et al. and Borukhov et al. [90, 29] to the size effects, because of two main reasons: First, and foremost, it is preferable to start with simple formulations that capture the essential physics while remaining analytically tractable, as we are mainly interested in new qualitative phenomena. Second, it is not clear to us how well the liquid-state theories would perform at large, time-dependent voltages, since they are (at least in some cases) based on perturbative methods around an equilibrium reference state, which may not even exist, say, in presence of an AC electric field.

A quick outline of this chapter is as follows: In section 5.2, we derive the modified Poisson Nernst-Planck (MPNP) equations, using the free energy obtained by [90, 29] to derive the modified PB equations (MPB). Instead of minimizing the free energy \( F \) we first compute the chemical potentials from the equation (5.7). Then we describe the electrolyte dynamics by linear response relations described by equations (5.2), (5.3). As a result, we end up with the promised MPNP equations which include steric corrections to the standard Nernst Planck equation that become increasingly important as the concentration field gets large. We continue in section 5.3 by setting up and investigating the numerical solutions of our modified PNP equations for the problem of parallel plate blocking electrodes. In section 5.4, we follow the same lines as in [13], and establish our earlier conclusions (including the electric circuit picture) about electrical double layers in chapter 4 by a rigorous asymptotic analysis. We also calculate higher order corrections to the thin double layer limit, and check a posteriori the validity of the leading order approximation. Finally, we close in section 5.5 by some comments and possible future directions for research.

5.2 Derivation of Modified PNP Equations

In this section, we derive the modified PNP equations as outlined in the introduction. For simplicity, let us restrict ourselves to the symmetric \( z : z \) electrolyte case. We also assume that the permittivity \( \varepsilon \) is constant in the electrolyte. In the mean-field approximation, the total free energy, \( F = U - TS \), can be written in terms of the local electrostatic potential \( \psi \) and the ion concentrations \( c_\pm \). Following [29], we write the electrostatic energy contribution \( U \) as

\[
U = \int d\mathbf{r} \left( -\frac{\varepsilon}{2} |\nabla \psi|^2 + zec_+ \psi - zec_- \psi \right) \tag{5.8}
\]

The first term is the self-energy of the electric field for a given potential applied to the boundaries (which acts as a constraint on the acceptable potential fields), the next two terms are the
electrostatic energies of the ions. The entropic contribution (the steric effects) can be modeled as [29]

\[ -TS = \frac{kT}{a^3} \int dr \{c_+a^3 \ln (c_+a^3) + c_-a^3 \ln (c_-a^3) \]
\[ + (1 - c_+a^3 - c_-a^3) \ln (1 - c_+a^3 - c_-a^3) \} \]

where we have assumed for simplicity that both types of ions and solvent molecules have the same size \(a\). The first two terms are the entropies of the positive and negative ions, whereas the last term is the entropy of the solvent molecules. It is this last term that penalizes large ionic concentrations.

Requiring that the functional derivatives of this free energy \(F\) with respect to \(\psi\) and \(c_\pm\) be respectively zero and constant chemical potentials \(\mu_\pm\) (the Lagrange multipliers for the conserved number of particles of each kind), Borukhov et al. [29] obtain the modified PB equation

\[ \nabla^2 \psi = \frac{zec_0}{\varepsilon} \frac{2 \sinh \left( \frac{ze\psi}{kT} \right)}{1 + 2\nu \sinh^2 \left( \frac{ze\psi}{2kT} \right)} \] (5.10)

Here we go one step further and derive MPNP by calculating the chemical potentials \(\mu_\pm\) from (5.7), yielding

\[ \mu_\pm = \frac{\delta F}{\delta c_\pm} \]
\[ = \pm z\varepsilon \psi + kT(\ln c_\pm - \ln (1 - c_+a^3 - c_-a^3)) \]

and as a reasonable form for the dynamics we postulate

\[ \frac{\partial c_\pm}{\partial t} = \nabla \cdot (b_\pm c_\pm \nabla \mu_\pm) \] (5.12)

This form which is classical for close to equilibrium transport is already an approximation, as it neglects cross-terms in the mobility matrix (i.e. that the gradients in \(\mu_-\) can induce a current of positive ions). Further, we now assume that the mobilities for each type of ions are the same, and equal to \(b = b_+ = b_-\) which is consistent with the assumption that they have the same effective size \(a\). A final approximation is that we take this value \(b\) to be constant, and in particular insensitive to the crowding that can occur in the electric double layers. All these approximations will be further discussed and challenged in subsequent work, but we proceed for the time being with the present simpler version, which is a first attempt to incorporate steric effects in the dynamics. As the electric fields adjust almost instantaneously to minimize the electrostatic energy, the Poisson equation assumes the form

\[ \frac{\delta F}{\delta \psi} = \varepsilon \nabla^2 \psi + z\varepsilon (c_+ - c_-) = 0 \] (5.13)
The equations (5.12) yield modified Nernst-Planck equations:

\[
\frac{\partial c_\pm}{\partial \tau} = D \nabla^2 c_\pm - \frac{D}{k_BT} z e \nabla \cdot (c_\pm \nabla \psi) + a^3 D \nabla \cdot \left( \frac{c_\pm \nabla (c_+ + c_-)}{1 - c_+ a^3 - c_- a^3} \right)
\]

where \(D = kTb\) is the common diffusion coefficient. As mentioned before, the extra last term is a correction due to the finite size effects. Considered together the above set of equations are modified Poisson-Nernst-Planck equations (MPNP), which is our simplest proposal for a dynamic description that incorporate steric effects. As in the standard case, this set of equations are completed by appropriate boundary conditions. In particular, we consider in this chapter that no reactions take place at the surface (blocking electrodes) so that no-flux boundary conditions

\[
D \nabla c_\pm = 0
\]

hold for the ions. We write the boundary condition for the potential by accounting as before for the possible presence of a thin insulating layer of fixed capacitance \(C_s\). This leads to a mixed boundary condition

\[
\psi(n = 0) = \psi_{\text{electrode}} + \lambda_S \frac{\partial \psi}{\partial n}(n = 0)
\]

where \(\psi_{\text{electrode}}\) is the applied potential at the electrode which is reduced by the insulating layer to \(\psi_{n=0}\) at the surface of the electrolyte (where MPNP starts to be applied). \(\lambda_S = \varepsilon/C_s\) is a measure of the thickness of this layer. Here, \(n\) is the normal direction to the surface pointing into the electrolyte.

### 5.3 Model Problem for the Analysis of the Dynamics

In order to gain some insight into the ramifications of the extra term we introduced into PNP, we now turn back to the basic model problem discussed in reference [13]. Namely, as shown in Fig. 5-1, we consider the effectively one-dimensional problem of an electrolyte cell bounded by two parallel walls (at \(x = \pm L\)), filled with a \(\text{z:z}\) electrolyte, at concentration \(c_0\), and across which a step voltage of amplitude (2V) is suddenly applied at \(t = 0\). We further assume that no Faradaic reactions are induced at the electrodes surface. We formulate MPNP in this setting, and then compare some numerical solutions of MPNP to those of PNP. In the next section we will focus on the case where the double layer thickness \(\lambda_D = (2e^2c_0/\varepsilon k_BT)^{-1/2}\) is much smaller than the (half) cell thickness \(L\).

First off, we note that, in this simple geometry, the gradients are replaced by \(\frac{\partial}{\partial x}\) and the derivative with respect to surface normal is replaced by \(\frac{\partial}{\partial x}\) at \(x = -L\), and by \(-\frac{\partial}{\partial x}\) at \(x = L\). Following [13], we cast the MPNP equations in dimensionless form using \(L\) as the reference length scale, and \(\tau_c = \lambda_D L/D\) as the reference time scale, thus time and space are represented by \(t = \tau D/\lambda_D L\) and \(\tilde{x} = x/L\). The problem is better formulated through the reduced variables \(c = \frac{1}{2c_0} (c_+ + c_-)\) for the local salt concentration, \(\rho = \frac{1}{2c_0} (c_+ - c_-)\) for the local charge density, and \(\phi = z e \psi/kT\) for the electrostatic potential. The solution is determined by three dimensionless parameters: \(\nu = z e V/kT\), the ratio of the applied voltage to thermal
Figure 5-1: Sketch of the model problem (from Ref. [13]). A voltage $2V$ is suddenly applied to a dilute, symmetric, binary electrolyte between parallel-plate, blocking electrodes separated by $2L$.

Voltage, $\epsilon = \lambda_D/L$, the ratio of the Debye length to the system size, $\delta = \lambda_S / \lambda_D$ introduced in section 4.2 which measures the surface capacitance, and finally a new parameter quantifying the role of steric effects $\nu = 2a^3c_0$, the effective volume fraction of the ions at no applied voltage. After dropping the tildes from the variable $x$, the dimensionless equations take the form

$$\frac{\partial c}{\partial t} = \epsilon \frac{\partial}{\partial x} \left( \frac{\partial c}{\partial x} + \frac{\partial \phi}{\partial x} + \frac{\nu c}{1 - \nu c} \frac{\partial c}{\partial x} \right)$$

$$\frac{\partial \rho}{\partial t} = \epsilon \frac{\partial}{\partial x} \left( \frac{\partial \rho}{\partial x} + \frac{\partial \phi}{\partial x} + \frac{\nu \rho}{1 - \nu c} \frac{\partial c}{\partial x} \right)$$

$$-\epsilon^2 \frac{\partial^2 \phi}{\partial x^2} = \rho$$

with completely blocking boundary conditions at $x = \pm 1$,

$$\frac{\partial c}{\partial x} + \rho \frac{\partial \phi}{\partial x} + \nu \frac{c}{1 - \nu c} \frac{\partial c}{\partial x} = 0$$

$$\frac{\partial \rho}{\partial x} + \frac{\partial \phi}{\partial x} + \nu \frac{\rho}{1 - \nu c} \frac{\partial c}{\partial x} = 0$$

in addition to (5.15), which reads
\[
\phi \pm \delta \epsilon \frac{\partial \phi}{\partial x} = \pm \nu \tag{5.18}
\]

at \( x = \pm 1 \), where again \( \delta \) measures the effective thickness of the surface insulating layer. Because it is impossible to satisfy all the boundary conditions when \( \epsilon = 0 \), the limit of vanishing screening length, \( \epsilon \to 0 \), is singular. The total diffuse charge near the cathode, scaled by \( 2\varepsilon c_0 L \), is

\[
q(t) = \int_{-1}^{0} \rho(x, t) dx \tag{5.19}
\]

The dimensionless Faradaic current, scaled to \( 2\varepsilon c_0 D/L \), is

\[
j_F = \frac{\partial \rho}{\partial x} + c \frac{\partial \phi}{\partial x} + \nu \frac{\rho}{1 - \nu c} \frac{\partial c}{\partial x}. \tag{5.20}
\]

We have numerically solved these equations for various values of the dimensionless parameters. As a complete description of this large parameter space would be very lengthy, we focus on a few situations for which we provide plots meant to illustrate the differences brought in by accounting for steric effects. We therefore also plot the outcome of classical PNP in the same situations (which correspond to \( \nu = 0 \) in the equations). Of course a systematic difference is that with the MPNP neither the concentration \( c \) nor the charge density \( \rho \) ever overcome the steric limit \( 1/\nu \).

For sake of readability of the figure, we start in Fig.5-2 with untypically large values for both the \( \epsilon = 0.1 \) and \( \nu = 0.25 \). The potential is ten times larger than the thermal voltage \( \nu = 10 \). The map of the concentration and charge density are given for different instants after the application of the potential drop. Build-up of the double layers, and the consequent depletion of salt in the bulk are visible. The MPNP solution stays bounded by \( 1/\nu \) as promised, whereas the PNP solution blows up exponentially. A consequent observation is that salt depletion in the bulk is weaker with the MPNP, whereas with the classical PNP bulk concentrations drop to small values even for this moderate potential (\( \sim 0.25 \) \( V \) in dimensional units). Of course, this is also a consequence of the large \( \epsilon \).

For a simulation with more realistic values, we have taken \( \nu = 40 \) (corresponding to \( 1 \) \( V \) in dimensional units), and \( \epsilon = \nu = 0.01 \). The corresponding solutions are plotted at nondimensional times \( t = 0, 0.5, 1, 2, 4, 6, 8, 10, ..., 50 \) in Fig.5-3. Figure 5-3(a) shows the bulk concentration dynamics, whereas Figure 5-3(b) focuses on the double layer near the boundary at \( x = -1 \). The MPNP solution again stays bounded by \( 1/\nu = 100 \). The PNP solution is not plotted as it blows up in the double layer to about \( \cosh(40) \approx 10^{17} \) times the bulk value (itself consequently very small), requiring subtle numerical methods. With the MPNP, the charge build up of the double layer first proceeds as it would with the PNP until concentrations close to the threshold \( 1/\nu \) are reached. Thereafter, charging proceeds by growth of the double layer thickness at almost constant density.

### 5.4 Asymptotic Analysis

In this section, we adapt to the MPNP equations introduced here the asymptotic analysis presented in [13] for PNP equations in the limit of thin double layers. We show rigorously
that the key properties of the charging dynamics remain the same, namely, at leading order the boundary layer acts like a capacitor with a total surface charge density $\tilde{q}(t)$ that changes in response to the Ohmic current density $\tilde{j}(t)$ from the bulk. However, the expressions for the capacitance of the double layer, and the diffusive flux from the bulk into the double layer do change, as we already discussed in chapter 4.

5.4.1 Inner and Outer Expansions

Adopting the notation in [13], we seek regular asymptotic expansions in $\epsilon$. We observe that the system has the following symmetries about the origin

$$c(-x, t) = c(x, t), \quad \rho(-x, t) = -\rho(x, t), \quad \phi(-x, t) = -\phi(x, t)$$

therefore, we consider only $-1 < x < 0$.

The outer solution, in the bulk, is denoted by a bar accent, and the expansion takes the form

$$c = \bar{c}(x, t) = \bar{c}_0 + \epsilon \bar{c}_1 + ...$$

It is easy to check that $\bar{c}_0 = 1$, $\bar{\rho}_0 = 0$ and $\bar{\phi}_0 = \bar{j}(t)x$ as a direct consequence of our choice for the time scale as $\tau_c$. As to the inner solutions (i.e. $x \approx -1$), we remove the singularity of
Figure 5-3: The numerical solution (for dimensionless average salt concentration \( c(t) \)) to the MPNP system is plotted at the dimensionless times \( t = 0, 0.5, 1, 2, 4, 6, 8, 10, ..., 50 \). In (b), we plot the same solution, zooming into the double layer. The parameters \( \epsilon = \nu = 0.01 \) are still large, but comparatively realistic.

equation (5.16) by introducing \( \xi = (1 + x)/\epsilon \). Then, we obtain

\[
\begin{align*}
\epsilon \frac{\partial c}{\partial t} &= \frac{\partial}{\partial \xi} \left( \frac{\partial c}{\partial \xi} + \rho \frac{\partial \phi}{\partial \xi} + \frac{\nu c}{1 - \nu c} \frac{\partial c}{\partial \xi} \right) \\
\epsilon \frac{\partial \rho}{\partial t} &= \frac{\partial}{\partial \xi} \left( \frac{\partial \rho}{\partial \xi} + c \frac{\partial \phi}{\partial \xi} + \frac{\nu \rho}{1 - \nu c} \frac{\partial c}{\partial \xi} \right) \\
-\frac{\partial^2 \phi}{\partial \xi^2} &= \rho
\end{align*}
\]  

(5.21) \hspace{1cm} (5.22) \hspace{1cm} (5.23)

for which, we can seek regular asymptotic expansions

\[ c = \tilde{c}(\xi, t) = \tilde{c}_0 + \epsilon \tilde{c}_1 + ... \]

Matching inner and outer solutions in space involves the usual van Dyke conditions, e.g.

\[ \lim_{\xi \to \infty} \tilde{c}(\xi, t) = \lim_{x \to -1} \tilde{c}(x, t) \]

which implies \( \tilde{c}_0(\infty, t) = \tilde{c}_0(-1, t), \tilde{c}_1(\infty, t) = \tilde{c}_1(-1, t), \) etc. As seen from equations (5.21)-(5.23), there are no terms with time derivatives at leading order. This quasiequilibrium occurs, because the charging time \( \tau_\epsilon \) is much larger than the Debye time \( \tau_D = \lambda_D^2 / D \), which is the characteristic time scale for the local dynamics in the boundary layer. Consequently, the leading
order solution is the "equilibrium"
\[ \tilde{\phi}_0 = \frac{\cosh \tilde{\Phi}_0}{1 + \nu \left( \cosh \tilde{\Phi}_0 - 1 \right)}, \quad \tilde{\rho}_0 = \frac{-\sinh \tilde{\Phi}_0}{1 + \nu \left( \cosh \tilde{\Phi}_0 - 1 \right)} \]
where the excess voltage relative to the bulk
\[ \tilde{\Phi} = \tilde{\phi}(\xi, t) - \tilde{\phi}(-1, t) \sim \tilde{\Phi}_0 + \epsilon \tilde{\Phi}_1 + ... \]
satisfies the modified PB equation at leading order
\[ \frac{\partial^2 \tilde{\Phi}_0}{\partial \xi^2} = \frac{\sinh \tilde{\Phi}_0}{1 + \nu \left( \cosh \tilde{\Phi}_0 - 1 \right)} \quad (5.24) \]
with \( \tilde{\Phi}_0(\infty, t) = 0 \), and \( \tilde{\Phi}_0(0, t) = \tilde{\zeta}(t) \), the dimensionless zeta potential, which varies as the diffuse layer charges. Applying matching to the electric field, we obtain
\[ \frac{\partial \tilde{\phi}(\infty, t)}{\partial \xi} \sim \epsilon \frac{\partial \tilde{\phi}(-1, t)}{\partial x} \Rightarrow \frac{\partial \tilde{\phi}_0(\infty, t)}{\partial \xi} = 0 \quad (5.25) \]
and therefore an integration of (5.24) yields
\[ \frac{\partial \tilde{\Phi}_0}{\partial \xi} = -\text{sign}(\tilde{\Phi}_0) \sqrt{\frac{2}{\nu} \ln \left( 1 + \nu \left( \cosh \tilde{\Phi}_0 - 1 \right) \right)} \quad (5.26) \]

5.4.2 Time-dependent matching
So far we have found that both the bulk and the boundary layers are in quasiequilibrium, which apparently contradicts the dynamic nature of the charging process. This is reconciled by noting once more that the boundary condition for the inner solution involves the quantity \( \tilde{\zeta}(t) \), which varies in response to the diffusive flux from the bulk. Motivated by the physics, we consider the total diffuse charge, which has the scaling \( q(t) \sim \epsilon \tilde{q}(t) \), where
\[ \tilde{q}(t) = \int_{0}^{\infty} \tilde{\rho}(\xi, t) d\xi \sim \tilde{q}_0 + \epsilon \tilde{q}_1 + \epsilon^2 \tilde{q}_2 + ... \quad (5.27) \]
Taking a time derivative, and using (5.22) together with the no flux boundary condition (5.17), we obtain
\[ \frac{d\tilde{q}}{dt}(t) = \lim_{\xi \to \infty} \frac{1}{\epsilon} \left( \frac{\partial \tilde{\rho}}{\partial \xi} + \tilde{c} \frac{\partial \tilde{\phi}}{\partial \xi} + \frac{\nu \tilde{\rho}}{1 - \nu \tilde{c}} \frac{\partial \tilde{c}}{\partial \xi} \right) \]
\[ \sim \lim_{x \to -1} \left( \frac{\partial \tilde{\rho}}{\partial x} + \tilde{c} \frac{\partial \tilde{\phi}}{\partial x} + \frac{\nu \tilde{\rho}}{1 - \nu \tilde{c}} \frac{\partial \tilde{c}}{\partial x} \right) \]
where we applied matching to the flux densities. Substituting the regular expansions of inner and outer solutions yield a hierarchy of matching conditions. At leading order, we have

\[
\frac{d\tilde{q}_0}{dt}(t) = \tilde{j}_0(t)
\]

which, being a balance of \(O(1)\) quantities, is reassuring us that we have chosen the correct timescale. This is the key equation which tells us that at leading order, the double layer behaves like a capacitor, whose total surface charge density \(\tilde{q}_0\), changes in response to the transient Faradaic current density, \(\tilde{j}_0(t)\), from the bulk.

**5.4.3 Leading Order Dynamics**

Using equations (5.23),(5.25) and (5.26), the integral in (5.27) can be performed at leading order to yield

\[
\tilde{q}_0(t) = -\text{sign}(\tilde{\varphi}_0) \sqrt{\frac{2}{\nu} \ln[1 + \nu(\cosh \tilde{\varphi}_0 - 1)]}
\]

Then the Stern boundary condition, eq.(5.18), yields

\[
\tilde{\varphi}_0 + \delta \text{sign}(\tilde{\varphi}_0) \sqrt{\frac{2}{\nu} \ln[1 + \nu(\cosh \tilde{\varphi}_0 - 1)]}
= \tilde{j}_0(t) - v = \tilde{\Psi}_0
\]

where \(\tilde{\Psi}(t) = -\nu - \tilde{\varphi}(-1, t) \sim \tilde{\Psi}_0 + \epsilon \tilde{\Psi}_1 + \ldots\) is the total voltage across the compact and the diffuse layers. Equation (5.30) results in higher \(\tilde{\varphi}_0\) than its classical PNP (or PB) counterpart

\[
\tilde{\varphi}_0 + 2\delta \sinh(\tilde{\varphi}_0/2) = \tilde{\Psi}_0
\]

because the left hand side of (5.30) is always smaller than the left hand side of (5.31) for any given \(\tilde{\varphi}_0\). In both formulas, the first term (i.e. \(\tilde{\varphi}_0\)) is the voltage drop over the diffuse layer whereas the second term (i.e. \(-\delta \tilde{q}_0\)) is the voltage drop over the Stern layer. For high applied voltages, the standard model assigns exponentially bigger proportions of that voltage to the Stern layer, whereas the modified theory predicts a balanced distribution. For more details, see chapter 4 section V.

Substituting into the matching condition (5.28), we obtain an ordinary initial value problem

\[
-C_0(\tilde{\Psi}) \frac{d\tilde{\Psi}_0}{dt} = \tilde{\Psi}_0 + v, \quad \tilde{j}_0(0) = v
\]

where

\[
C_0 = -\frac{\frac{d\tilde{q}_0}{d\tilde{\Psi}_0}}{\frac{1}{|\sinh \tilde{\varphi}_0|} \sqrt{\frac{2}{\nu} \ln[1 + \nu(\cosh \tilde{\varphi}_0 - 1)]}} + \delta
\]
is the differential capacitance for the double layer as a function of its voltage. This has a completely different behaviour than its counterpart in [13], namely

$$
\tilde{C}_0 = \frac{1}{\text{sech}(\tilde{\zeta}_0/2) + \delta}
$$

(5.34)
evenly at higher \(\tilde{\zeta}_0\). As \(\tilde{\zeta}_0 \to \infty\), our differential capacitance \(\tilde{C}_0^{\nu=0}\) \(\sim (\sqrt{\frac{2}{\nu}} \tilde{\zeta}_0 + \delta)^{-1} \to 0\), in contrast to \(\tilde{C}_0^{\nu=0}\), the differential capacitance given by (5.34), which tends to \(\delta^{-1}\) (see chapter 4 for more details). Thus, at high zeta potentials, steric effects decrease the capacitance, possibly down to zero. Physically, this is because of the increasing double layer thickness as a result of excessive pile up of the ions coming from the bulk into the double layer (see Part 1).

Equation (5.33) is separable, and its solution can be expressed in the form

$$
\tilde{\Psi}_0 = \tilde{j}_0(t) - v = -F^{-1}(t)
$$

(5.35)

\[F(z) = \int_0^z \frac{\tilde{C}_0(u)}{v + u} \, du\]

(5.36)

Steric effects reduce the capacitance, and therefore \(F(z)\), which by formula (5.36) implies a faster relaxation process for the voltage difference \(\tilde{\Psi}_0\). In other words, the RC relaxation time is shortened (see chapter 4).

5.4.4 Neutral Salt Adsorption by the Double Layer

A natural consequence of reduced capacitance at the electrodes is the reduction of the amplitude of the diffusion layer in the bulk were the adsorbed salt in the double layer is extracted from. We now revisit some of the ideas in [13], and recalculate the neutral salt adsorption by the double layer. The excess ion concentration, \(c - c_0\), acquired by the double layers is accounted for by the diffusion from the bulk at \(O(\epsilon)\) or higher, as diffusion is absent at leading order. Following [13], we introduce the variable \(w(t) = \epsilon \tilde{w}(t)\), akin to \(q(t)\), which represents the excess amount of salt in the double layer:

$$
\tilde{w}(t) = \int_0^\infty \left[ \tilde{c}(\xi, t) - \tilde{c}_0(-1, t) \right] d\xi = \tilde{w}_0(t) + \epsilon \tilde{w}_1(t) + ...
$$

Taking a time derivative, we find

$$
\frac{d\tilde{w}_0}{dt}(t) = \lim_{\epsilon \to -\infty} \frac{1}{\epsilon} \left( \frac{\partial \tilde{c}}{\partial \xi} + \rho \frac{\partial \phi}{\partial \xi} + \frac{\nu \tilde{c}}{1 - \nu \tilde{c} \partial \xi} \right)
$$

$$
\sim \lim_{\epsilon \to -1} \left( \frac{\partial \tilde{c}}{\partial \xi} + \rho \frac{\partial \phi}{\partial \xi} + \frac{\nu \tilde{c}}{1 - \nu \tilde{c} \partial \xi} \right)
$$

(5.37)

Since \(\tilde{c} = 1 + \epsilon \tilde{c}_1 + ...\), at leading order \(\tilde{c} \sim 1\) and \(\frac{\partial \tilde{c}}{\partial x} \sim \epsilon \frac{\partial \tilde{c}_1}{\partial x}\), therefore (5.37) yields

$$
\frac{d\tilde{w}_0}{dt}(t) = \frac{1 - \nu}{\epsilon} \frac{d\tilde{w}_0}{dt}(t) = \frac{\partial \tilde{c}_1}{\partial x}(-1, t)
$$

(5.38)
which involves the new time variable
\[ \tilde{t} = \frac{\epsilon}{1 - \nu} t = \frac{\epsilon}{1 - \nu} \tau = \frac{\tau}{\tau_s} \]
scaled to bulk diffusion time, \( \tau_s = (1 - \nu) \frac{L^2}{D} \), which is slightly different from the time scale given in [13]. The salt uptake \( \tilde{w}(t) \) can be expressed in terms of an integral
\[
\tilde{w}(t) = \int_0^\infty \left( \frac{\cosh \tilde{\Phi}}{1 + \nu (\cosh \tilde{\Phi} - 1)} - 1 \right) d\xi
\]
\[
= \int_0^\infty \frac{\cosh \tilde{\Phi} - 1}{1 + \nu (\cosh \tilde{\Phi} - 1)} \frac{(1 - \nu) d\tilde{\Phi}}{\sqrt{2} \ln \left(1 + \nu \left( \frac{1}{\cosh \tilde{\Phi} - 1} \right)\right)}
\]  
(5.39)

with no obvious further simplification.

We now proceed to calculate the depletion of the bulk concentration during the double-layer charging. Note that the new time scale \( \tau_s \) introduced by (5.38) is the time scale for the first order diffusive dynamics in the bulk
\[
\frac{\partial \tilde{c}_1}{\partial \tilde{t}} = \frac{(1 - \nu)}{\epsilon} \frac{\partial \tilde{c}_1}{\partial \tilde{t}} = \frac{\partial^2 \tilde{c}_1}{\partial x^2}
\]  
(5.40)

As the source is defined by (5.38) in terms of gradients, an appropriate Green’s function can be obtained by taking Laplace transforms and using method of images as in [13], which leads to
\[
\tilde{c}_1(x, \tilde{t}) = -\int_0^\infty d\tilde{\ell} G(x, \tilde{t} - \tilde{\ell}) \frac{\partial}{\partial \tilde{t}} \left[ \tilde{w}_0 (\tilde{\ell} / \epsilon) \right]
\]  
(5.41)

where
\[
G(x, \tilde{t}) = \frac{1}{\sqrt{\pi \tilde{t}}} \sum_{m=-\infty}^{\infty} e^{-(x-2m+1)^2 / 4 \tilde{t}}
\]  
(5.42)

In the limit \( \epsilon \to 0 \), the initial charging process at the time scale \( \tau_c = O(\epsilon) \) is almost instantaneous, which is followed by the slow relaxation of the bulk diffusion layers. This limit corresponds to approximating the source terms in the integral in (5.41) to exist only in a small \( O(\epsilon) \) neighborhood of zero, or more explicitly
\[
\lim_{\epsilon \to 0} \tilde{c}_1(x, \tilde{t}) \simeq -G(x, \tilde{t}) \int_0^\infty d\tilde{\ell} \frac{\partial}{\partial \tilde{t}} \left[ \tilde{w}_0 \left( \frac{\tilde{\ell}}{\epsilon} \right) \right]
\]
\[
= -\tilde{w}_0 (\infty) G(x, \tilde{t}),
\]  
(5.43)

with
\[
\tilde{w}_0 (\infty) = \int_0^{f^{-1}(\nu)} \frac{\cosh \tilde{\Phi} - 1}{1 + \nu \left( \frac{1}{\cosh \tilde{\Phi} - 1} \right)} \sqrt{\frac{1}{2} \ln \left(1 + \nu \left( \frac{1}{\cosh \tilde{\Phi} - 1} \right)\right)}
\]  
(5.44)
where
\[ f(\zeta) = \zeta + \text{sign}(\zeta)\delta \sqrt{\frac{2}{\nu}} \ln (1 + \nu (\cosh \zeta - 1)). \] (5.45)

As expected from the underlying physics, and already explained in chapter 4 and illustrated in the plots of section III above, the formula (5.44) predicts smaller values for the depth of the bulk diffusion than its classical PNP (\(\nu = 0\)) counterpart. This difference is more pronounced at higher \(\nu\). Equation (5.43) is a simple approximation that describes two diffusion layers created at the electrodes slowly invading the entire cell. At first, they have simple Gaussian profiles

\[ \tilde{c}(x, t) \sim 1 - \frac{\epsilon \tilde{w}_0(\infty)}{\sqrt{\pi t}} \left[ e^{-(x+1)^2/4t} + e^{-(x-1)^2/4t} \right] \] (5.46)

for \(\epsilon \ll \tilde{t} \ll 1\). The two diffusion layers eventually collide, and the concentration slowly approaches a reduced constant value,

\[ \tilde{c}(x, t) \sim 1 - \epsilon \tilde{w}_0(\infty) \] (5.47)

for \(\tilde{t} \gg 1\), as we expect from the steady-state excess concentration from the double layers. Of course one expects that at large enough applied voltage, the above approximation breaks down, as the decrease in bulk concentration becomes significant and thus modifies the value of \(w\) in the double layer.

### 5.4.5 Validity of the Weakly Nonlinear Approximation

The first order solution consisting of the variables indexed by "0" is often referred to as the weakly nonlinear approximation, whose main feature is that the bulk concentrations are constant, namely \(\tilde{c} \approx \tilde{c}_0 = 1\) and \(\tilde{\rho} \approx \tilde{\rho}_0 = 0\). The system therefore is characterized only by the surface charge \(\tilde{q} \approx \tilde{q}_0\), or the double layer potential difference \(\tilde{\Psi} \approx \tilde{\Psi}_0\), which is governed by the nonlinear ODE in equation (5.32). This corresponds to modeling the problem by an equivalent circuit model with variable capacitance for the double layer, and constant bulk electrolyte resistance.

In order to understand when the weakly nonlinear approximation holds, we can compare the size of the next order approximation to the leading term. Although not a rigorous proof, one may argue that if \(\epsilon |c_1|\) is much smaller than \(\tilde{c}_0 = 1\), then leading order term is a good approximation to the full solution. We will get help from the approximations (5.46) and (5.47) to see if this is the case.

Seen in the light of equation (5.47), the assumption that the first correction is much smaller than the leading term requires that \(\nu_0 = \epsilon \tilde{w}_0(\infty) \ll 1\), in other words,

\[ \epsilon (1 - \nu) \int_0^{f_1(\nu)} \frac{\cosh \Phi - 1}{1 + \nu (\cosh \Phi - 1)} \frac{d\Phi}{\sqrt{2 \ln (1 + \nu (\cosh \Phi - 1))}} \ll 1, \] where \(f\) is given in (5.45). After a series of approximations, including \((1 - \nu) \approx 1, \delta = O(1), \text{ and } \zeta \gg 1\) or \(\nu \gg 1\), this becomes \(\epsilon \sqrt{\frac{2}{\nu}} \ln (1 + \nu \cosh v) \ll 1\). If \(\nu\) is not too close to zero (i.e. \(\nu \cosh v \gg 1\)), this is the same as \(2e^2 \nu / \nu \ll 1\). Putting the units back, we obtain

\[ 2 \frac{\lambda_D^2}{L^2 a^3 c_0} \frac{z e V}{kT} \ll 1 \] (5.48)
For a typical experiment with $\lambda_D = 10 \text{ nm}$, $L = 0.1 \text{ mm}$, $c_0 = 1 \text{ mM}$, $a = 5 \text{ Å}$, and at room temperature, this condition becomes $V \ll 188 \text{ Volts}$.

However, the weakly nonlinear dynamics breaks down at somewhat smaller voltages, because the neutral salt adsorption causes a temporary, local depletion of bulk concentration exceeding that of the final steady state. In our model problem, the maximum change in bulk concentration occurs just outside the diffuse layers at $x = \pm 1$, just after the initial charging process finishes at the same scale $t = O(1)$ or $\tilde{t} = O(\epsilon)$. Letting $\tilde{t} = \epsilon$, and $x = \pm 1$ in equation (5.46), we obtain the first two terms in the asymptotic expansion as

$$ c(\pm 1, \epsilon) = 1 - \sqrt{\frac{\epsilon}{\pi}} \tilde{w}_0(\infty). $$

At that time, the double layers have almost been fully charged, however the bulk diffusion has only had time to reach a region of length $O(\sqrt{\epsilon})$. So the concentration is depleted locally by $O\left(\frac{\epsilon}{\sqrt{\pi}}\right) = O(\epsilon)$, which is much more than the uniform $O(\epsilon)$ depletion remaining after complete bulk diffusion.

Therefore, in order for the time-dependent correction term to be uniformly smaller than the leading term, we need

$$ \sqrt{\frac{\epsilon}{\pi}} \tilde{w}_0(\infty) \ll 1. \quad (5.49) $$

By the same approximations as in (5.48), this yields $\frac{2\nu}{\sqrt{\pi} \nu} \ll 1$, or with units

$$ \frac{2}{\sqrt{\pi}} \frac{\lambda_D}{La^3c_0} \frac{zeV}{kT} \ll 1. \quad (5.50) $$

The corresponding threshold voltage is smaller than the former by a factor of roughly $\sim L/\lambda_D = \epsilon^{-1}$. For the same set of parameter as above $\lambda_D = 10 \text{ nm}$, $L = 0.1 \text{ mm}$, $c_0 = 1 \text{ mM}$, $a = 5 \text{ Å}$, and at room temperature, this condition gives $V \ll 0.033 \text{ Volts}$. Thus according to this criterion, the weakly nonlinear approximation easily breaks down, and one may need to consult to the full MPNP system for an understanding of the electrolyte dynamics.

A more accurate understanding into the condition (5.49) is gained by the numerical study of the function $w$. The curves on which $\sqrt{\epsilon w} = 1$ (i.e. $\epsilon = w^{-2}$) are plotted in Fig.5-4 for various values of $\nu$ (here we dropped the somewhat arbitrary factor $\sqrt{\pi}$ in (5.49)). The weakly nonlinear approximation holds to the south-west of these curves when $\sqrt{\epsilon w} \ll 1$. The criterion given by the inequality (5.50) corresponds to the asymptotic behaviour of those curves as $\nu$ tends to infinity.

To observe that this is the case numerically, we have also compared the charging dynamics given by the weakly nonlinear approximation to that of the full MPNP solution in Fig.5-5, with the parameters $\epsilon = \nu = 0.01$. When the parameters were to the south-west of the curve $\sqrt{\epsilon w} = 1$, as in case (c), the match was perfect. In the other cases, the weakly nonlinear approximation did not do as well, it was particularly off for case (b), when the product $\sqrt{\epsilon w}$ yielded the highest number. In case (a), the agreement was off by a constant shift, whereas in case (d), the situation improved over time. This is because $\epsilon w$ is still small for case (d), although $\sqrt{\epsilon w}$ is not, and therefore weakly nonlinear approximation is still valid for the final state of the system.

To summarize, if an accurate description of the system at all times is desired, then $\sqrt{\epsilon w} \ll 1$
is the appropriate criterion, however it may suffice to have just $\varepsilon w << 1$ to be able to predict the eventual steady state by the weakly nonlinear model.

### 5.5 Conclusions

As an extension of the modified PB approach, we have derived modified PNP equations, which may be of help when the thin double layer approximation fails. Using this new set of equations, we have revisited the model problem of the step charging of a cell with parallel blocking electrodes. In addition, we have confirmed through asymptotic analysis the hypotheses stated in chapter 4 regarding the MPB double layer model. We have also investigated the limits of the thin double layer approximation as well as higher order corrections.

The MPNP system proposed is a natural extension of one of the two models introduced in chapter 4, namely the MPB model based on an approach originally due to [21, 54, 6, 60]. One can similarly construct other MPNP equations from other MPB models such as the composite diffuse-layer model also introduced in chapter 4. However the discontinuous structure of the latter leads to a complex formalism with discontinuities, improper for implementation in complex geometries, whereas the one presented here has a smooth behavior and is therefore much more broadly applicable.

We expect that the MPNP equations presented here, or other simple variations with different modifications of the chemical potentials or free energy, will find many applications. They are no more difficult to use than the classical PNP equations, which are currently ubiquitous in the modeling of electrochemical systems. Especially at large voltages, the MPNP equations are much better suited for numerical computations, since they lack the exponentially diverging
Figure 5-5: Four case studies on the validity of the weakly nonlinear approximation. No stern capacitance is included ($\delta = 0$). In Fig.5-4(b), we show $\sqrt{\nu} = 1$ curve for the particular value $\nu = 0.01$, and corresponding locations of the four case studies shown. The comparison of the charge $q(t)$ stored in the half cell computed by (i) the PNP (ii) the weakly nonlinear approximation corresponding to the mPNP. The match in (c) is good as expected, and the match in (b) is off by several factors, again as expected. In cases (a) and (d), the curves run close but they are clearly separated.

concentrations predicted by the PNP equations, which are difficult to resolve. Of course, those same divergences are also clearly unphysical, while the MPNP equations predict reasonable ion profile for any applied voltage.

Future research directions include the application of the presented framework to many other settings including the response of the simple electrolytic cell considered here to various systems with time-dependent applied voltages of strong amplitudes. In particular, driving an electrochemical cell or AC electro-osmotic pump at rather large frequencies should be a selective way of checking the validity/use of equations such as the one put forward here because dynamical effects are exacerbated in such situations.
Chapter 6

Steric Effects in Induced Charge Electrokinetics

In this chapter, we investigate the crowding effects in the electrokinetic theory, which originally motivated this thesis work. We find important qualitative implications, some of which might explain outstanding experimental puzzles. The two main application areas are the electrophoretic mobility of colloidal particles and the flow rate in microfluidic ACEO pumps. In the following chapters, we apply the weakly nonlinear theory with the steric double layer capacitances to obtain our results.

6.1 Electrophoretic Mobility

The electrophoretic mobility of a colloidal particle, denoted by \( b_{ep} = \frac{U}{E} \), refers to the particle velocity per unit electric field. Under the assumption of fixed surface charge (i.e. nonpolarizable particles), this ratio -in theory- is a material constant for a homogeneous particle with uniformly charged thin double layers, and does not depend on the shape, size or the background electric field. For polarizable particles, this picture changes completely: the mobility depends on all those three factors, thanks to the induced charges created on the particle surface by the applied electric fields. For a neutral particle, the acting of the electric field on its own induced charge results in quadrupolar flow around the particle with a velocity scaling \( U \propto R E^2 \), where \( R \) is the particle size.

For charged particles, the induced charge effects modify the electrophoretic mobility. For weak electric fields \( E \ll kT/eR \), Dukhin has calculated the first correction to the mobility as

\[
b_{ep}(E) = \frac{\varepsilon_b}{\eta_b} (\zeta_0 - \frac{3}{8} \frac{C_d'(\zeta_0)}{C_d(\zeta_0)} (ER)^2 + ...)
\]

for an ideally polarizable sphere. In the linear theory, when the differential capacitance is constant, the polarization effects decouple and the mobility is not affected by the ICEO flows. However, the differential capacitance is not constant in general, and this might either enhance or diminish the electrophoretic mobility. For example, the PB theory, where \( C_d(\zeta_0) = \frac{e}{\lambda_D} \cosh(\frac{ze\zeta_0}{e\lambda_D}) \), predicts reduced mobility as \( dC_d/d\zeta > 0 \). For the steric MPB theories suggested in the chapter 4 and 5, however, the \( C_d \) is non-monotonous, therefore the mobility can increase or decrease
with the electric field depending on the particle zeta potential $\zeta_0$. While the steric theories agree with the dilute solution theory and predict reduced mobilities at small zeta potentials $\zeta_0 < kT/e$, they imply the opposite trend at large $\zeta_0 >> kT/e$.

The steric effects become more pronounced in a large electric field, $E >> kT/eR$, even for small particle zeta potentials. The dilute solution theory, using the formalism of [178], predicts that the mobility of a charged, ideally polarizable, spherical particle vanishes exponentially in the limit $E >> kT/eR$

$$b_{ep}^{PB} \sim 3\frac{e}{\eta} \sinh\left(\frac{2e\zeta_0}{2kT}\right)ERe^{-3zeER/4kT}. \quad (6.2)$$

This can be understood in simple physical terms as follows: A large electric field induces an exponentially large antisymmetric charge density, which dominates the symmetric (uniform) original charge density on the particle. Since the zeta potential $\zeta_0$ depends only logarithmically on the total (original plus induced) charge density, it becomes practically antisymmetric as the bigger part of the total charge is induced by the electric field. Needless to say, this almost antisymmetric $\zeta_0$ leads to no motion.

The steric model follows the PB theory at low electric fields, but predicts a completely different trend at large electric fields $E >> kT/eR$: the mobility

$$b_{ep}' \sim \frac{e}{\eta} \sqrt{\frac{3\nu kT R}{4ze}} \quad (6.3)$$

starts to increase like $\sqrt{E}$ after an initial decline, as shown in Fig.6-1 $($v = 0 curve$)$. This is because the crowding effects reduce the double layer charging, thus precluding the antisymmetry of total double layer charge distribution on the particle. In addition, the electrokinetic slip depends more sensitively on the double layer charge density: additional charges would make the diffuse layer thicker, and cause noticeably more slip, in fact, the slip coefficient $\zeta$ depends superlinearly on the double layer charge density $q$. Because of this reason, the mobility of the particle goes up at large electric fields. In the following subsections, we give a detailed analysis of these results.

### 6.1.1 The Standard Problem

For an ideally polarizable particle under the influence of a uniform, time-dependent electric field $E = E_0\hat{z}$, the appropriate boundary conditions are

$$\psi \sim -E \cdot r \text{ as } r \to \infty \quad (6.4)$$

and, at the surface of the particle,

$$C(\psi_0 - \psi) \frac{d\psi}{dt} = n \cdot (\sigma \nabla \psi). \quad (6.5)$$

Here, $C(\psi)$ is the differential capacitance of the double layer, $n$ is the normal pointing inside the electrolyte, $\sigma$ is the electrolyte conductivity and $\psi_0$ is the particle potential, determined from the conservation of charge

$$Q = \int q(\psi_0 - \psi)dA, \quad (6.6)$$
where \( q(\zeta) = - \int_0^\infty C'(\psi) d\psi \) is the surface charge density on the particle. After solving these two electrostatic problems, the electrokinetic slip on the particle is computed using Helmholtz-Smoluchowski’s (HS) formula

\[
\mathbf{u}_s = -\frac{\varepsilon}{\eta} \mathbf{E}_// = \frac{\varepsilon}{\eta} (\psi - \psi_0) \mathbf{E}_//
\] (6.7)

and entered into the hydrodynamic problem. For most cases of interest, the solution is viscous and only the Stokes problem is solved (see chapter \( 3 \)).

For a steady problem, the electrostatic problem for \( \psi \) decouples from that of \( \psi_0 \), and by replacing equation (6.5) with the Neumann boundary condition \( \mathbf{n} \cdot (\nabla \psi) = 0 \), where we assumed \( \sigma \) is constant as in the weakly nonlinear formulation.

For a spherical particle centered at origin with radius \( R \), this problem has an analytical solution

\[
\psi = -E_0 z (1 + \frac{R^3}{2\pi^3})
\]

therefore, the potential on the particle surface is

\[
\psi = -\frac{3}{2} E_0 z = -\frac{3}{2} E_0 R \cos \theta,
\]

where \( \theta \) is the azimuthal angle. Therefore, the constraint (6.6) turns into

\[
\int_0^\pi q(\psi_0 + \frac{3}{2} E_0 R \cos \theta) 2\pi R^2 \sin \theta d\theta = Q = 4\pi R^2 \bar{q}
\] (6.8)

For an uncharged sphere, the solution to this equation is \( \psi_0 = 0 \) by symmetry.

The Stokes problem simplifies dramatically for a spherical particle as well. The results of Stone and Samuel [181] imply that the electrophoretic velocity of the particle, with a prescribed slip \( \mathbf{u}_s \) is simply the surface averaged velocity

\[
\mathbf{U} = -\frac{1}{4\pi R^2} \oint \mathbf{u}_s d\mathbf{A} = -\frac{1}{2} \int_0^\pi \mathbf{u}_s(\theta) \sin \theta d\theta
\]

The second line holds only in the special case \( \mathbf{u}_s = \mathbf{u}_s(\theta) \), that is, the slip velocity depends only on the azimuthal angle \( \theta \). Another simplification results from combining this last equation with the HS slip formula (6.7)

\[
\mathbf{U} = -\frac{1}{2} \int_0^\pi \frac{\varepsilon}{\eta} (\psi - \psi_0) \mathbf{E}_// \sin \theta d\theta
\]

\[
= -\frac{1}{2} \int_0^\pi \frac{\varepsilon}{\eta} (-\frac{3}{2} E_0 R \cos \theta - \psi_0) \mathbf{E}_// \sin \theta d\theta
\] (6.9)

By symmetry, we know that the particle moves only in the \( \hat{z} \) direction, therefore it suffices to
consider only the $\hat{z}$ component of $E_{//}$, which yields

\[ U = -\frac{1}{2} \int_0^\pi \frac{\varepsilon}{\eta} (-\frac{3}{2} E_0 R \cos \theta - \psi_0) (-\frac{3}{2} E_0 \sin^2 \theta) \sin \theta d\theta \]

\[ = -\frac{\varepsilon}{\eta} E_0 \psi_0 \frac{3}{4} \int_0^\pi \sin^3 \theta d\theta = -\frac{\varepsilon}{\eta} E_0 \psi_0 \]

Interestingly, the classical zeta potential of the sphere, $\zeta_{c kep}$, is equal to its electrostatic potential $\psi_0$ determined by (6.8). This is also true for a "cylindrical" particle. Note that these results are not a consequence of the linear electrophoresis theorem discussed in chapter 2, which deals with particles of constant surface charge.

Induced charge electroosmosis is a nonlinear phenomenon, and even with the assumption of constant double layer capacitance, the electroosmotic flow has an $E^2$ scaling. However, this nonlinear scaling does not always imply nonlinear particle mobility. More precisely, the surface zeta potential $\zeta = \psi_0 - \psi$ scales with $E_0 R$, therefore the characteristic flow velocity around the particle is $U_0 = \frac{\varepsilon}{\eta} E_0^2 R$. On the other hand, the zeta $\zeta_{c kep}$ measuring the electrophoretic velocity of the particle is strongly dependent on the particle charge $Q$. In the linear theory, where $q(\zeta) = -\zeta$, the equation (6.8) implies $\psi_0 = Q/4\pi R^2 \equiv \bar{q}$, leading to fixed particle mobility $\mu_{ep} = U/E_0 = \frac{\varepsilon}{\eta} \frac{Q}{4\pi R^2}$. This would imply that spherical particles could be separated electrophoretically only by their charge density, and not by size.

6.1.2 PB Theory: I. Mobility of a Spherical Colloid

In this section, we investigate the aforementioned predictions of the PB theory for a spherical colloid and verify our calculations through Dukhin’s expansion (6.1).

The dimensionless charge density in the PB theory is given by $q = -2 \sinh \left( \frac{\zeta}{2} \right)$, where $q$ is scaled by $2ze\lambda_D Rc_0$, and $\zeta$ by $kT/ze$. Plugging this into the equation (6.8), we obtain

\[ \int_0^\pi -\sinh(\frac{\psi_0}{2} + \frac{3}{4} E_0 R \cos \theta) \sin \theta d\theta = -2 \sinh \left( \frac{\zeta_0}{2} \right) \]

where $\zeta_0 = -2 \sinh^{-1}(\bar{q}/2)$ is the particles zeta potential at zero electric field, and it occurs in the formula (6.1) as the first term, which equals the limiting mobility as the field strength vanishes, as there are no induced charges in this limit. This integral can be calculated by the change of variables $u = \cos \theta$ to yield

\[ -2 \sinh \left( \frac{\zeta_0}{2} \right) = \frac{4}{3E_0 R} \left[ \cosh(\frac{\psi_0}{2} + \frac{3}{4} E_0 R) - \cosh(\frac{\psi_0}{2} - \frac{3}{4} E_0 R) \right] \]

\[ = -\frac{8}{3E_0 R} \sinh(\frac{3}{4} E_0 R) \sinh(\frac{\psi_0}{2}) \]

which gives us the result

\[ \psi_0 = 2 \sinh^{-1} \left( \frac{3E_0 R}{4} \frac{\sinh \left( \frac{\zeta_0}{2} \right)}{\sinh \left( \frac{3}{4} E_0 R \right)} \right) \] (6.10)
Note that, in the limit $E_0 R \to 0$, this would yield $\psi_0 = \zeta_0$.

### 6.1.3 PB theory: II. Weak and Strong Electric Fields

We can derive the formula (6.1) by expanding for the weak electric fields $E_0 R << kT/ze$:

$$\sinh\left(\frac{\psi_0}{2}\right) = \frac{3E_0 R}{4} \frac{\sinh\left(\frac{\zeta_0}{2}\right)}{\sinh\left(\frac{3}{4}E_0 R\right)} = \frac{\sinh\left(\frac{\zeta_0}{2}\right)}{1 + \frac{3}{32}(E_0 R)^2 + \ldots}$$

$$= \sinh\left(\frac{\zeta_0}{2}\right) - \cosh\left(\frac{\zeta_0}{2}\right) \left[ \frac{3}{32} \tanh\left(\frac{\zeta_0}{2}\right) (E_0 R)^2 \right] + \ldots$$

$$= \sinh\left(\frac{1}{2} \left[ \zeta_0 - \frac{3}{8} (E_0 R)^2 \frac{d}{d\zeta} \log(\cosh(\frac{\zeta}{2})) \right] + \ldots \right)$$

and therefore we recover the first correction by taking the inverse sinh of both sides. While (6.10) covers all electric field ranges, note that (6.1) is more general in the sense that $C$ does not need to come from the PB theory. We will later derive the formula for the case of general double layer capacitance $C$.

At large electric fields, the argument of the inverse hyperbolic sinh in (6.10) decays rapidly to zero, therefore we can approximate the potential $\psi_0$ as

$$\psi_0 \sim 3E_0 R \sinh\left(\frac{\zeta_0}{2}\right) \exp\left(-\frac{3}{4}E_0 R\right)$$

which yields (6.2) when dimensionalized.

### 6.1.4 General Steric Models

For a general model of the double layer charge density, given through $q = q(\psi_0 - \psi)$, we use the substitution $\psi = \psi_0 + \frac{3}{2} E_0 R \cos \theta$ in (6.8) to obtain

$$\frac{1}{3E_0 R} \int_{\psi_0 - \frac{3}{2} E_0 R}^{\psi_0 + \frac{3}{2} E_0 R} q(\tilde{\psi}) d\tilde{\psi} = q(\zeta_0)$$

(6.11)

In the small electric field limit, we can expand the integrand in Taylor Series as

$$q(\zeta_0) = \frac{1}{3E_0 R} \int_{\psi_0 - \frac{3}{2} E_0 R}^{\psi_0 + \frac{3}{2} E_0 R} \left[ q(\psi_0) + q'(\psi_0)(\tilde{\psi} - \psi_0) + \frac{1}{2} q''(\psi_0)(\tilde{\psi} - \psi_0)^2 + \ldots \right] d\tilde{\psi}$$

$$= q(\psi_0) + \frac{1}{6E_0 R} q''(\psi_0) \int_{\psi_0 - \frac{3}{2} E_0 R}^{\psi_0 + \frac{3}{2} E_0 R} (\tilde{\psi} - \psi_0)^2 d\tilde{\psi} + \ldots$$

$$= q(\psi_0) + q'(\psi_0) \left[ \frac{3}{8} q''(\psi_0) (E_0 R)^2 \right] + \ldots = q(\psi_0) + \frac{3}{8} q''(\psi_0) (E_0 R)^2 + \ldots$$

hence we recover the first term in the expansion (6.1) by recalling that $q'(\psi_0) = -C(\psi_0)$. 118
If the electrolyte is symmetric in terms of both ion charges and size effects, then the surface charge density \( q \) is odd in double layer voltage, and the integral in (6.11) can be simplified to

\[
\frac{1}{3E_0R} \int_{\frac{3}{2}E_0R-\psi_0}^{\frac{3}{2}E_0R+\psi_0} q(\tilde{\psi}) d\tilde{\psi} = \bar{q} = q(\zeta_0)
\]

In the large \( E_0R \) limit, we can expand the Taylor Series for \( q \) around \( \frac{3}{2}E_0R \) under the assumption that \( \psi_0 \) remains smaller compared to \( \frac{3}{2}E_0R \), which yields \( \psi_0 = \frac{3}{2}E_0Rq(\zeta_0)/(q(\frac{3}{2}E_0R) + \frac{1}{3}C'(\frac{3}{2}E_0R)q^3 + ...). \) The leading term, which corresponds to assuming that \( q \) is approximately linear in the range of the integral, amounts to

\[
\psi_0 = \frac{3}{2}E_0R\frac{q(\zeta_0)}{q(\frac{3}{2}E_0R)}
\] (6.12)

For the Gouy-Chapman theory, this implies a rapid decay due to the exponential dependence of \( q \) on the field strength. When a Stern layer is added, the capacitance becomes constant at high voltages, therefore \( q \) becomes a linear function of double layer voltage. The eventual mobility is then a constant, and is given by

\[
b_{ep} = \frac{\varepsilon}{\eta} \psi_0 = \frac{\varepsilon}{\eta} \frac{\bar{q}}{C_{stern}}
\]

While nonzero, this would still mean that the particle mobility is independent of its size.

A different prediction is made by the MPB model introduced in chapter 4. Since, in this
theory, the double layer charge have a square root dependence on voltage, we end up with the trend given earlier in (6.3), that is, the mobility eventually increases like $\sqrt{E_0 R}$. This behaviour persists even when a Stern layer is added into the MPB model.

The steric model also predicts a different type of regime for the extremely highly charged particles. As we mentioned earlier in the introduction, when a spherical particle is highly charged so that there is already crowding even in the absence of an electric field, its mobility does not initially decrease with an applied electric field, as shown in Fig.6-2. This result may not be relevant as it is hard for a particle to acquire such large charge densities on its surface without an external driving force.

### 6.1.5 Simple Asymmetric Electrolyte

We predict even more dramatic effects with asymmetric electrolytes, where positive and negative ions have different effective sizes. The simplest MPB model assumes two different sizes $a_\pm$, and

$$q(\psi) = \begin{cases} q^{\nu+}(\psi) & \text{when } \psi \leq 0 \\ q^{\nu-}(\psi) & \text{when } \psi > 0 \end{cases}$$

where $\nu_\pm = 2a_\pm^3 c_0$. This is a good approximation at all voltages, because (i) at low voltages, the charge densities given by $\nu_\pm$ agree with the PB theory and each other (ii) at high voltages the double layer is dominated by the counterions, so it does not matter much if we are inaccurate in describing the size of co-ions.

A surprising prediction of the steric theory is that even uncharged spherical particles would
move under applied electric fields. If the positive ions are smaller (larger), the particle moves in the same (opposite) direction as the electric field. The basic mechanism can be understood as follows: When the applied field polarizes the particle, it draws, say, an amount $+q_{\text{pol}}$ of charges from the northern hemisphere to the southern hemisphere of the particle. Since negative ions are larger, they screen this positive surface charge less effectively and need higher potentials on the double layers to summon the required amount of ions. In addition, they start to cover up more of the particles surface area. Both of those factors tip the balance in the surface-generated electrokinetic slip in favor of the negatively charged double layers, pushing the particle in the direction of the electric field.

In concentrated solutions with highly uneven ion sizes, this effect could be so strong that a charged particle could move in the opposite direction than predicted alone by the charge of the particle, as seen in Fig. 6-3. All of those predictions await experimental verification. Also keep in mind that the above results rely on the HS slip formula, which cannot explain the concentration dependence of electro-osmotic flows. We suspect that the HS formula breaks down at large voltages and/or concentrations, and propose modified slip formulas for electrokinetic slip in the next section, where we visit this problem in more detail.

### 6.2 Steric Implications in ACEO

The study of microfluidic ACEO pumps, where electrokinetic slip on the electrodes is utilized to generate fluid motion, is a current area of research and the topic of this section. In this approach, micro-electrodes are placed close to each other (gaps on the order of the size of electrodes), and therefore large electric fields can be generated by applying a few volts across them. As a steady voltage difference would be screened and eventually generate no flow, the use
of an AC source is a necessity. This also has the advantage of reducing the harmful chemical reactions at the electrode.

### 6.2.1 Flow Reversal in Asymmetric Planar ACEO Pump

A recent ACEO pump design [146] involves a planar array of flat electrode pairs of unequal widths and gaps. The idea is that the larger electrode collects more charge and drives a stronger flow in "its" direction. At low voltages, or low frequencies, this pump acts as expected. However, at high voltages and high frequencies, Ramos et al. [146] found that this asymmetric array of planar electrodes generates flow in the opposite direction than expected, which was later confirmed by experiments of Studer et al. [183].

This phenomenon is not captured by either of the linear or PB theories. Numerical simulations of the Ramos' geometry with the standard linear theory predicts only a single peak in flow rate at all voltages. The PB theory does even worse: It still predicts a single peak, but the exponentially large double layer capacitance and thus slower charging dynamics shifts it to much lower frequencies, conflicting with the experiments. It has been suggested that the flow reversal is caused by Faradaic charging at the electrodes, but the simulations with Butler-Volmer reaction kinetics were able to predict flow reversal only at low frequencies [134]. The significance of those reactions diminish at high frequencies, at which flow reversal takes place in experiments.

Steric effects on the double layer capacitance provide a possible explanation for high fre-
Figure 6-5: Average slip velocity as a function of frequency for three different models at \( V = 100\frac{AT}{\varepsilon} \approx 2.5 \) Volts for the ACEO pump in Fig.6-4. The PB theory, like the linear model, predicts a single peak, which takes place at very low frequencies out of the range of the plot. The MPB model with \( \nu = 0.01 \) predicts a reduced peak velocity and high frequency flow reversal.

Frequency flow reversal of ACEO pumps. Recall that steric effects imply a monotonous differential double layer capacitance, which decreases at large voltages, or equivalently, high surface charge densities. This means that the charging gets increasingly faster at highly charged surfaces. Therefore, the smaller electrode, which in general has a larger charge density (but less overall charge), is able to charge more promptly and pump harder at higher frequencies than the bigger electrode.

Sample plots of flow rate as a function of frequency for the steric theory along with linear and PB theories are shown in Fig.(6-5). The linear theory at least predicts the correct order of magnitude for the flow rate, and the approximate optimal frequency, whereas the PB theory misses both completely. As discussed, the steric MPB model reduces the peak flow rate, and introduces flow reversal at high frequency just like observed in the experiments. However, a rather large effective ion size (few nm) needs to be used in the MPB theory to generate reasonable predictions that compare well with experimental data: To obtain \( \nu = 0.01 = 2a^3c_0 \) at \( c_0 = 1mM \), we need \( a = \sqrt[3]{\frac{\nu}{2c_0}} \approx 2nm \). Smaller but more realistic \( \nu \) values yield a shift in the peak towards smaller frequencies which does not agree with the experiments. This shortcoming of the steric theory can be remedied by using more accurate models for the finite size effects, such as the Carnahan-Starling (CS) model for hard sphere interactions. For more details on this study, we refer to [182].
Figure 6-6: Contour plots of the average slip velocity scaled by $U_0 = \frac{\varepsilon V_0^2}{\eta L}$ as a function of the frequency $\omega$ and the applied voltage $V_0$ using (a) the MPB model with $\nu = 0.0001$, and (b) the MPB model with $\nu = 0.01$, (c) the PB model, (d) the PB model with $\delta = 0.1$. The white contours designate zero flow rate. At small voltages, the flow rate has only a single peak, and the model can be approximated with the linear theory, while flow reversal develops in MPB models at high voltages for high frequencies.
6.2.2 Nonplanar ACEO pumps

The asymmetric planar array of electrodes are certainly not the most efficient ACEO pumps: the large and the small electrodes are creating flows in the opposite directions and the larger ones win. If only we could make both electrodes pump in the same direction. This type of thinking led Bazant and Ben [9] to suggest a stepped electrode structure, which pumps faster up to an order of magnitude than the planar electrodes in simulations. In this structure, the electrode sections that pump in the desired direction are elevated. From another point of view, the opposing electrode sections are recessed and they create fluid rolls which in the end help the pumping done by elevated electrodes.

Indeed, Urbanski et al. [189, 190] experimentally confirmed the superior efficiency of the 3D stepped pump design: Several times faster flows than the planar pumps are easily attained, and the high-frequency flow reversal is completely suppressed when large enough steps are used. However, the experiments show surprising flow dependence on the forcing frequency: if the step height is not small, two distinct peak-frequencies appear.

In this section, we present results of a few simulations of the 3D pumps using the steric MPB models. Unfortunately, our simulations fail to capture the double-peak phonemenon. The MPB models yield only a single peak, similar to the linear theory. We further suggested that the double-peaks may correspond to two different optimal charging times, possibly as a result of differently sized ions, however, we were not able to show this in our simulations with the simple asymmetric MPB models.

First, we take the geometry used in [189], where \( L_1 = 15\mu m, L_2 = 5\mu m, G = 5\mu m \), and \( H_1 = 2.7\mu m \). The length scale is usually chosen to be the gap length, \( L = G = 5\mu m \), and the unit frequency \( \omega_0 = \frac{\pi}{L} \). The flow rate is scaled by the unit velocity \( U_0 = \frac{V_0 L^2}{\pi} \) (note that this depends on \( V_0 \)). Periodic boundary conditions are imposed on the vertical boundaries at the ends of the region in the Fig.6-7(b), and the gap between two electrode plates is always \( G \). Since we have had success with fairly large \( \nu \) in the case of planar pumps, we choose \( \nu = 0.01 \).
Figure 6-8: Simulations of the 3D pumps with the MPB model using $\nu = 0.01$ for the dimensions (a) $L_1 = 15\mu m$, $L_2 = G = 5\mu m$, $H_1 = 2.7\mu m$ as in [189] and (b) $L_1 = L_2 = G = 5\mu m$, $H_1 = 6.6\mu m$ as in [190]. The MPB model correctly predicts the high frequency flow reversal for case (a), but fails to capture the double-peaked flow rate/frequency profile.

in order to see if the steric effects play a role, and simulate the pump using COMSOL software. As shown in Fig.6-8(a), the model cannot predict the double peaks in the data of [189] which appear at high voltages, but we do again capture the high-frequency flow reversal albeit at larger voltages than the data. However, this flow reversal may not result from steric effects as this behavior is also predicted by linear models for such 3D pumps in [190]. In addition, the experiments in [189] are conducted with de-ionized water, so steric effects might be minimal.

The second geometry is a more symmetrical one with $L_1 = 5\mu m$, $L_2 = 5\mu m$, $G = 5\mu m$, and varying heights $H_1$ between 0 and 9.9$\mu m$, which are considered in [190] using a 3$\mu M$ KCl solution. We illustrate the simulation results with $H_1 = 6.6\mu m$ in Fig.6-8(b) for the MPB model with $\nu = 0.01$. The high frequency flow reversal is now suppressed, which agrees with the experiments, because the step height is large enough so that a "fluid conveyor belt" is created. In this case, there is not sufficient (if any) electrokinetic slip pulling in the reverse direction at any applied frequency. Similar results are predicted by linear models [190], so finite size effects may not be important in those experiments, especially since a very dilute solution is used. Therefore the double-peak phenomena might have some other explanation than steric effects.

### 6.3 Concentration Effects

The ACEO micropumps reveal a strong decay of the electroosmotic flow with increasing concentrations, so much so that all flow practically vanishes around the critical concentration $c_c = 10mM$. A logarithmic dependence of the form $U \propto \log(c_c/c_0)$ can be predicted from the limited experimental data with KCl [183, 107, 14], but there is also support for this trend from ICEO flows around metal particles and ICEP motion of Janus particles (see table 2.1).
The simplest theory that predict some concentration dependence is the Stern Layer model. As discussed in section 4.5, the compact layer takes on most of the voltage drop in the large voltage limit. In the PB theory, we have \( \Psi_D + \frac{2kT}{ze} \delta C_s \sinh\left(\frac{ze\Psi_D}{2kT}\right) = \Psi \), and therefore as \( ze \gg kT \)

\[
z\varepsilon / kT \approx \frac{2kT}{ze} \log\left(\frac{ze\varepsilon / kT}{kT}\right) - \frac{kT}{ze} \log\left(\frac{2z^2e^2c_0}{kTC_s}\right)
\]

where we used \( \delta = \lambda_D C_s / \varepsilon \), \( C_s \) being the Stern capacitance. The diffuse layer potential drop \( \zeta \), which determines the electrokinetic slip in the usual Helmholtz-Smoluchowski (HS) slip formulation (6.7), depends logarithmically on the bulk concentration \( c_0 \), and the dependence is in the right direction (reduced slip with increasing concentration). At large voltages, only a logarithmically small part of the potential drop contributes to the electrokinetic slip. The rest of the potential drop takes place across the compact layer, which might lead to dielectric breakdown of water or reactions as we point out in in section 4.5. If we include the steric effects as given by the MPB theory, the compact layer no longer takes on such a big portion of the voltage drop, and we conclude that the slip must be larger. This is illustrated in Fig.6-9, where we plot the diffuse layer voltage drop in terms of total double layer voltage for both PB and MPB theories at three different concentrations. It is interesting to note that \( \zeta \) increases with the effective ion size \( a \), while it decreases with bulk concentration \( c_0 \). Thus, with the Stern layer model, steric effects may enhance or reduce the electrokinetic slip, depending on whether they are caused by large ions or a large number of ions.

In the rest of this section, we will analyze the effect of variations in the dielectric constant \( \varepsilon \) and viscosity \( \eta \) within the diffuse layer on the created electrokinetic slip. Let us formulate the
Figure 6-10: The electrokinetic zeta as a function of diffuse layer voltage drop in Lyklema's [114] viscoelectric theory.

generalized HS slip formula (2.30) as

$$b = \int_0^{\Psi_D} \frac{\varepsilon}{\eta} d\psi = \frac{\varepsilon_b}{\eta_b} \zeta_{ek}$$  \hspace{1cm} (6.14)

where the electrokinetic slip is given by $u_s = bE_//$. In the original HS Slip formulation, which we have used in this chapter so far, $\varepsilon$ and $\eta$ are constants and the electrokinetic zeta potential $\zeta_{ek}$ is equal to the double layer voltage drop $\Psi_D$ (which is sometimes denoted by $\zeta$, without a bar, in this thesis). At large voltages, when there is a significant pile-up of ions in the double layer, $\zeta_{ek}$ should be smaller than $\Psi_D$ in absolute value because not only $\varepsilon$ decreases (due to alignment of water dipoles) but also $\eta$ increases (due to viscoelectric effects) within the diffuse layer. While it is quite difficult to measure how $\varepsilon$ and $\eta$ change in a crowded diffuse layer accurately, the qualitative effects of their behaviour can still be investigated through simple models.

Lyklema [114] and Lyklema and Overbeek [117] focused on the viscoelectric effects (i.e $\eta = \eta(E)$) in water to modify the HS slip formula. Those effects exist when the solvent molecules are polarizable, and independent of any ions (if they exist at all) in the solution. Assuming a viscosity dependence of the form $\Delta\eta \propto E^2$ and using the PB theory, the integral in (6.14) becomes

$$\zeta_{ek} = \frac{kT}{\varepsilon} \int_0^{\varepsilon \Psi_D/kT} \frac{d\psi}{1 + Kc_0 E^2} = \frac{kT}{\varepsilon} \int_0^{\varepsilon \Psi_D/kT} \frac{d\psi}{1 + 4Kc_0 \sinh^2 \left( \frac{\varepsilon \psi}{2kT} \right)}$$  \hspace{1cm} (6.15)

where $K$ is a constant. Here, the concentration dependence enters through the electric field (which is scaled inversely by the Debye length $\lambda_D$), and $K$ only depends on the properties of
the solvent. Lyklema evaluated this integral and predicted that, at large potentials, \( \zeta_{ek}(\Psi_D) \) reaches a plateau the value of which decreases with the bulk concentration \( c_0 \), as shown by solid curves in Fig.6-10. He also collected supporting experimental data from the literature, summarized in Fig. 3 in [114].

However, this flattening nature of the \( \zeta_{ek} \) in (6.15) may be an artifact due to the unphysical divergence of the electric field in PB theory. If the finite size effects are included using the Bikerman’s MPB theory, then the integral in (6.15) becomes unbounded in the large \( \Psi_D \) limit. Nevertheless, as shown in Fig.6-10, \( \zeta_{ek} \) becomes practically flat for any voltage range of interest, unless we take unrealistically large values for the effective ion size \( a \), like \( a = 2nm \). This is not as absurd as it sounds, given the success of large effective ion sizes in the previous section on the ACEO pumps.

Lyklema has estimated \( K \approx 3.05(nm)^3 \) for water so that the integral (6.15) converges quickly, and even at low concentrations \( \zeta_{ek} \) does not exceed a few \( kT/ze \) (e.g. at 1mM, the maximum is around \( 5kT/ze \)). In contrast, much higher \( \zeta_{ek} \) (up to \( 30kT/ze \)) values are inferred in recent experiments [14]. In addition, the viscoelectric model only takes into account the properties of solvent molecules, and hence fails to capture any dependence on the chemical characteristics of the ion species. This contradicts even the data shown by Lyklema himself in Fig.3 of his paper [114], where the electrophoretic mobilities depend on the type of electrolyte.

We argue that the diffuse layer consists mostly of the counterions, and strong interactions between the ions would play a greater role than the properties of water molecules. In the following subsections, we propose alternative mechanisms which could give way to similar results for the electrokinetic slip.

6.3.1 Composite Diffuse-Layer Model Revisited

In the composite diffuse-layer model introduced in chapter 4, we assume that the concentrations depend on the electrical potential as

\[
c_{\pm} = \min\left\{ c_0 e^{\mp z e \psi / k T}, \frac{1}{a^3} \right\}
\]

Within the double layer, this implies a composite inner region \( 0 \leq x \leq l_c \) where \( c_+ \) or \( c_- \) equals the maximum concentration \( c_{max} = \frac{1}{a^3} \), and a diffuse region where PB holds. In terms of electrokinetics, the important question is how the composite layer contributes, if at all, to the electrokinetic slip. This is related to how the ratio \( \varepsilon/\eta \) varies in the double layer. In the usual HS electrokinetic slip formula, we assume \( \varepsilon \) and \( \eta \) are constant everywhere, so the inner composite layer slips just as easily as the outer diffuse layer, but this is highly questionable. On the other end of the spectrum, we may propose that the composite layer is stuck to the electrode surface and does not slip at all. This may be the result of condensed ions forming a Wigner crystal[166] of like charges. In addition, if we still assume that \( \varepsilon/\eta \) is constant in the diffuse portion of the double layer, we obtain that the electrokinetic zeta potential \( \zeta_{ek} \) is given by

\[
\zeta_{ek} = sign(\Psi_D) \min\left\{ -\frac{kT}{z e} \ln \left( c_0 a^3 \right), |\Psi_D| \right\}
\]
In other words, double layer potentials larger than \( \zeta_{ek, \text{max}} = -\frac{kT}{\varepsilon e} \ln \left( c_0 a^3 \right) \) do not contribute to the electrokinetic slip.

Surprisingly, this simple model already captures the logarithmic dependence on the concentration to some extent. At large voltages, the crowding limit is always reached, and we have \( \zeta_{ek} = \pm \zeta_{ek, \text{max}} = \pm \frac{kT}{\varepsilon e} \ln \left( \frac{c_{\text{max}}}{c_0} \right) \) where \( c_{\text{max}} = \frac{1}{a^3} \) is both the maximum attainable concentration and the saturation value when the flow completely vanishes. There is a problem with this approach, however. If we equate \( c_{\text{max}} = 1/a^3 \) with \( c_c = 10mM \), we obtain \( a \approx 5.5nm \), which is unrealistically high and not even theoretically achievable because it corresponds to the space full of only one type of ions and a bulk volume fraction that is larger than unity: \( 2c_0 a^3 = 2 > 1 \), which is impossible. The largest value of \( a \) that is consistent with the MPB theory is \( a = 1/\sqrt{2}c_0 \) (so that \( 2c_0 a^3 = 1 \)), and even that does not give zero electrokinetic slip.

### 6.3.2 Modified Slip Formulae using MPB

The abrupt change of permittivity and viscosity in the composite diffuse layer model is unphysical, and it may also bring in unnecessary computational challenges in higher dimensional problems. Luckily, it is easy to develop models with similar qualitative behaviour in the MPB world. The ratio \( \varepsilon/\eta \) shall decrease in the double layer, although we do not know exactly how. As a very crude attempt, we postulate the formula

\[
\frac{\varepsilon}{\eta} = \frac{\varepsilon_b}{\eta_b} \left[ 1 - \min\{1, \left| \frac{\rho}{\rho_c^\pm} \right| \} \right]^\beta,
\]

where \( \alpha \) and \( \beta \) are free exponents, and \( \rho_c^\pm \) is the critical absolute charge density when the viscosity diverges, which can be expressed as an effective ion spacing for viscosity divergence \( a_c^\pm \) as \( \rho_c^\pm = \frac{|iz_\pm|}{a_c^\pm} \). This distance could be smaller or larger than the steric ionic spacing \( a \).

There is a neat expression for the choice \( \alpha = \beta = 1 \) when \( |\rho_c^\pm| \geq |\rho_{\text{max}}^\pm| \):

\[
\zeta_{ek} = \Psi_D - \frac{1}{\left| \rho_c^\pm \right|} \int_0^{\Psi_D} \rho d\psi = \Psi_D - \frac{1}{\left| \rho_c^\pm \right|} p (\Psi_D),
\]

where \( p \) is defined by (A.3). In the case of MPB models of chapter 4, this is given by

\[
\zeta_{ek} = \Psi_D - sgn(\Psi_D) \frac{|\rho_{\text{max}}^\pm| kT}{\varepsilon e} \ln \left( 1 + 4c_0 a^3 \sinh^2 \left( \frac{ze \Psi_D}{2kT} \right) \right).
\]

In the limit of point-like ions, \( a \to 0 \), or small double layer voltages \( \Psi_D \to 0 \), this formula reduces to the original HS formula \( \zeta_{ek} = \Psi_D \). Therefore we can envision the the second term in equation (6.18) as a steric correction to the electrokinetic slip. Even for dilute solutions with small ions, this correction becomes important at large enough double layer voltages.

If \( \rho_c^\pm = |\rho_{\text{max}}^\pm| \), then this model resembles the composite diffuse layer model with no slip contribution from the condensed layer. Although there is not a clear border between the condensed and diffuse regions in the MPB models, almost all (> %99) the slip is created by the less dense parts (\( c < 0.99c_{\text{max}} \)) of the double layer. At large voltages, \( \zeta_{ek} \) flattens out at near
its maximum
\[ \zeta_{ek, \text{max}} = -\frac{kT}{ze} \ln \left( \frac{c_0 a^3}{c_0} \right) = \frac{kT}{ze} \ln \left( \frac{c_{\text{max}}}{c_0} \right) \]

just like in the composite diffuse layer model, but with a smooth transition, as shown in Fig. 6-11(a). Similar results can be obtained with other MPB models in which counterions form nearly uniform, non-slipping condensed layers near the maximum concentration \( c_{\text{max}} \).

It is a different story when \( \rho_c^+ > |\rho_{\text{max}}^+| \). The condensed layers then contribute to the electrokinetic slip, and since their thickness grows indefinitely with increasing voltage, the electrokinetic zeta potential \( \zeta_{ek} \) is not bounded above by a maximum, but grows linearly with a limiting slope of \( (1 - \frac{|\rho_{\text{max}}^+|}{|\rho_c^+|}) \) at large \( \Psi_D \).

If \( \rho_c^- < |\rho_{\text{max}}^-| \), then the equation (6.17) becomes

\[ \zeta_{ek} = \max_{0 < \psi < \Psi_D} \left[ \psi - \frac{1}{|\rho_c^+|} p(\psi) \right] \]

In this case, the shear viscosity blows up before steric saturation so that some of the non-condensed diffuse layer is also laterally immobile. The resulting \( \zeta_{ek}(\Psi_D) \) is also like the composite layer model, only now with \( c_{\text{max}} \) replaced by \( \rho_c^+ / ze \). However, the differential capacitance is still governed by the original \( c_{\text{max}} = 1/a^3 \).

Regardless of what values \( \rho_c^+ \) and \( \rho_{\text{max}}^+ \) take on, the electroosmotic flow rate would depend on the concentration logarithmically \( U \propto \log (c_{\text{max}} / c_0) \) at large voltages when \( \rho_c^+ \) is achieved. This is illustrated for the MPB model of (6.18) with \( \rho_c^+ = |\rho_{\text{max}}^+| \) in Fig. 6-11(b). The electrokinetic zeta potential does not vanish at any concentration unless \( \rho_c^+ = 0 \) in which case there is no flow at any concentration. Therefore the complete flow saturation (i.e. \( \zeta_{ek} = 0 \) at a critical concentration \( c_c \)), if it really happens, is not predicted by this theory.

**Logarithmic Concentration Dependence**

The steric MPB model with the general Helmholtz-Smoluchowski formula of the form

\[ \zeta_{ek} = \frac{\eta_b}{\varepsilon_b} \int_0^{\Psi_D} \frac{\varepsilon}{\eta} \left( \frac{|\rho|}{|\rho_c^+|} \right) d\psi \]

always predicts a logarithmic concentration dependence or weaker at large potentials \( \Psi_D >> 1 \). The only assumption we need to show this is that the derivative of \( \frac{\varepsilon}{\eta} \) is bounded (this does not preclude divergent \( \eta \)).

Consider a concentration profile with bulk \( c_0 \) and total voltage drop \( \Psi_D \). We want to perturb this profile by increasing \( c_0 \) to \( c_0 + \Delta c_0 = c_0 e^\Delta \), and decreasing \( \Psi_D - \Delta \). We will show that

\[ \zeta_{ek}(c_0, \Psi_D) \approx \frac{\varepsilon_b}{\eta_b} \Delta + \zeta_{ek}(c_0 e^\Delta, \Psi_D - \Delta) + O\left( \frac{\varepsilon_b}{\eta_b} \frac{c_0 e^{-\Psi_D}}{|\rho_c^+|} \right) \]

(6.20)

in the \( \Delta \to 0 \) limit. Assuming \( \Psi_D >> 1 \), and dropping the last term, this would give us

\[ \frac{\partial \zeta_{ek}}{\partial \Psi_D} - c_0 \frac{\partial \zeta_{ek}}{\partial c_0} = \frac{\varepsilon_b}{\eta_b} \]

131
Figure 6-11: (a) Comparison of $\zeta_{ek}$ for the CDL model and MPB models with different $\rho_c$ at $\nu = 0.01$ using (6.17). Also plotted is the $\nu = 0$ limit, i.e. the PB model. (b) Comparison of $\zeta_{ek} = \zeta_{ek}(\Psi_D)$ plots for $\nu = 0, 10^{-2}, 10^{-4}$ and $10^{-6}$ for $\rho_c = \rho_{\text{max}}$. Since $\nu = 2c_0a^3$, if the effective ion size $a$ is constant, $\zeta_{ek}$ decreases with increasing concentration at large voltage limit.

which implies

$$0 > \frac{\partial \zeta_{ek}}{\partial c_0} > -\frac{1}{c_0 \eta_b} \varepsilon_b$$

(6.21)

This last relation implies that the concentration dependence of $\zeta_{ek}$ is at most like $-\log(c_0)$.

In order to show that (6.20) holds, assume without loss of generality that $\Psi_D > 0$. With the steric MPB model, the perturbed counterion concentration profile is

$$\rho(c_0 e^\Delta, \psi - \Delta) = \frac{c_0 e^\Delta (e^{\psi - \Delta} - e^{-\psi + \Delta})}{1 + a^3 c_0 e^\Delta (e^{\psi - \Delta} + e^{-\psi + \Delta} - 2)} = \frac{c_0 (e^\psi - e^{-\psi + 2\Delta})}{1 + a^3 c_0 (e^\psi + e^{-\psi + 2\Delta} - 2e^{\Delta})}$$

where the potential $\psi$ varies between $\Delta$ and $\Psi_D$. Comparing with the original concentration profile, we find that

$$\delta p \equiv \int_0^{\Psi_D} |\rho(c_0 e^\Delta, \psi - \Delta) - \rho(c_0, \psi)| d\psi$$

(6.22)

$$= p(c_0 e^\Delta, \psi - \Delta) - p(c_0, \psi)$$

(6.23)

$$= \frac{1}{2a^3} \log \left( \frac{1 + a^3 c_0 e^\Delta (e^{\Psi_D - \Delta} + e^{-\Psi_D + \Delta})}{1 + a^3 c_0 (e^{\Psi_D} + e^{-\Psi_D})} \right)$$

(6.24)

$$\approx \frac{1}{2} \frac{c_0 e^{-\Psi_D} (e^{2\Delta} - 1)}{1 + a^3 c_0 (e^{\Psi_D} + e^{-\Psi_D})}$$

(6.25)
Therefore, in the $\Delta \to 0$ limit,

$$
\zeta_{ek}(c_0e^\Delta, \psi_D - \Delta) = \int_0^{\psi_D - \Delta} \frac{\varepsilon}{\eta} \left( \rho(c_0e^\Delta, \psi) \right) d\psi = \int_0^{\psi_D} \frac{\varepsilon}{\eta} \left( \rho(c_0e^\Delta, \psi - \Delta) \right) d\psi
$$

$$
\approx \int_0^{\psi_D} \frac{\varepsilon}{\eta} \left( c_-(c_0, \psi) \right) d\psi + O\left( \frac{c_0e^{-\psi_D} \Delta}{|\rho_c^\pm|} \right)
$$

$$
\approx \zeta_{ek}(c_0, \psi_D) - \int_0^{\Delta} \frac{\varepsilon}{\eta} d\psi + O\left( \frac{c_0e^{-\psi_D} \Delta}{|\rho_c^\pm|} \right)
$$

$$
\approx \zeta_{ek}(c_0, \psi_D) - \frac{\varepsilon_b}{\eta_b} \Delta + O\left( \frac{\varepsilon_b c_0e^{-\psi_D} \Delta}{|\rho_c^\pm|} \right)
$$

which justifies the approximation in (6.20). On the third line, when we have replace $c_-(c_0e^\Delta, \psi - \Delta)$ by $c_-(c_0, \psi)$, the error term $O\left( \frac{c_0e^{-\psi_D} \Delta}{|\rho_c^\pm|} \right)$ is bounded by $M(\delta p)$ where $M$ is an upper bound for the derivative of $\varepsilon\left( \frac{|p|}{|\rho_c^\pm|} \right)$ with respect to $\frac{|p|}{|\rho_c^\pm|}$. For $\varepsilon$ in (6.16), we can choose $M = \alpha\beta$. The error term approaches zero at large potentials, and therefore the equation (6.20) holds.

6.3.3 ACEO Pumps Revisited

In the previous section, the MPB theory was able to capture an important feature of the flow rate in asymmetric planar ACEO pumps: the high frequency flow reversal at large voltages. However, the same theory fails to predict the concentration dependence of the ACEO flow, it only predicts a shift in the frequency profile of the flow rate. Not only has such a shift not been observed in experiments, but the flow has been observed to depend strongly on the electrolyte concentration in the works of [183, 189, 190].

In this section, we attempt to use the modified HS (MHS) slip formulae of this section in the planar ACEO pump simulations. As expected, we are now able to capture the flow rate dependence on concentration to some extent. However, the MPB theory no longer predicts high frequency flow reversal with the MHS formulation for the electrokinetic slip. This is understandable as we proposed that the physical mechanism for the flow reversal was the charging of the small electrodes faster and more fully at large voltages. Those shorter and highly charged electrodes reach the steric limit (which is when the differential capacitance starts to decline) and rapidly form a condensed layer. While these condensed layers help the small electrodes dominate the large ones in the HS theory, they are immobile and do not contribute to the electrokinetic slip with the MHS formulae. As a result, no flow reversal is predicted.

The results are demonstrated in Fig.6-12 for the asymmetric ACEO pump of Fig.6-4 at an applied voltage of $V_0 = 100\frac{EF}{2\varepsilon}$. The effective ion size is taken to be $a = 2nm$, and the concentrations $c_0 = 1mM, 0.1mM$ and $0.01mM$ (corresponding to $\nu = 10^{-2}, 10^{-3}$ and $10^{-4}$ respectively) are analyzed. The frequency is scaled with $\omega_0 = \frac{P_D}{\nu^2}(c_0=1mM)$ (recall that the dimensionless frequency depends on the concentration through the Debye length). Notice how the modified HS formulae reduces the flow, especially for more concentrated solutions. There is only a single peak, no flow in the opposite direction. In the original HS theory, the flow rate depends weakly on the concentration, but in the wrong way: higher concentrations enhance the flow because of the lower differential capacitance. This effect seems small though, as the MPB
Figure 6-12: Flow rate as a function of frequency in the asymmetric ACEO pumps in MPB theory with the HS (solid lines) and MHS (dashed lines) formulae for the electrokinetic slip. The parameter $\nu$ takes on values of $10^{-2}, 10^{-3}$ and $10^{-4}$ corresponding to concentrations of 1mM, 0.1mM and 0.01mM respectively for $a = 2\text{nm}$.

differential capacitance is independent of the concentration in the large voltage limit.

The more striking effect is the shifting in the frequency axis with concentration, which is at work for both the HS and the MHS slip formulae. As the MPB capacitance becomes independent of the concentration at high voltages, the reason for this shifting behaviour is solely the reduced electrolyte resistance with increasing concentration. The resistance scales with $1/c_0$, and decreases the $RC$ charging time, causing the shift in the frequency profile. While having a sound theoretical basis, the shifting has not been observed clearly in the experiments. Speculatively, electrode reactions may create new ionic species that interfere with the electrolyte resistance, possibly rendering it independent of the original bulk concentration. Unless new effects like that are examined and put into the theory, we will continue to predict the unobserved shift in the flow rate as a function of frequency.

6.3.4 Colloids in Asymmetric Electrolytes Revisited

The asymmetry of ion sizes modifies the mobility of colloidal particles through inducing asymmetric differential capacitances as we have seen earlier in the chapter. However, we did not take into account the saturation of the electrokinetic zeta potential asymmetrically as a result of different ionic sizes. In other words, we continued to use the HS slip formula.

Apparently, this effect counteracts the nonlinear capacitance effect, but is not strong enough to reverse it, at least not for the case of spherical particles, which we consider here: Recall that under a large electric field, larger counterions pack at lower density and thus cover more surface than the smaller ions. This has a significant effect on mobility, as it means that the equator of the particle is covered by one type of ion and produces slip in one direction, as opposed to being neutral and producing no net slip in the symmetric case. The equatorial region of the particle
is where the most electrophoretic propulsion comes from, because the tangential electric field and the electrokinetic slip are both oriented in the right direction, and parallel to each other. As a result, this effect can be strong and moves the particle in the opposite direction to the larger ions that cover its equatorial belt.

In the MHS theory, however, there is an additional contrary effect: these larger ions produce less slip than their smaller counterparts, because they condense more easily into immobile composite layers at maximum concentration. However, it turns out that the conquest of the crucial equatorial region is more important than the smaller ions producing more slip around a pole.

Following the analysis in equations (6.4) to (6.9), the velocity of a polarizable spherical particle of radius \( R \) is given by

\[
U = \frac{1}{2} \varepsilon_b \int_0^\pi \zeta_{ek}(\psi - \psi_0)E_\parallel \sin \theta d\theta
\]

where the particle potential \( \psi_0 \) is determined from the equation (6.11). The \( x- \) and \( y- \) symmetries are still not broken, so we can still consider only the \( z \) component of the parallel electric field, which is \( E_\parallel \cdot \hat{z} = -\frac{3}{2}E_0 \sin^2 \theta \). Plugging in, and factoring out an \( E_0 \) gives us the mobility

\[
b_{ep} = \frac{3}{4} \varepsilon_b \int_0^\pi \zeta_{ek}(\psi - \psi_0) \sin^3 \theta d\theta
\]

The \( \sin^3 \theta \) function once more demonstrates how much of the contribution to mobility comes from the equatorial region around \( \theta = \frac{\pi}{2} \). A few plots of this formula are shown in Fig.6-13. The dashed curves are the mobility of a spherical particle in the HS theory with steric capacitances of the model of (6.13) with (a) \( \nu_- = 0.1 \) and \( \nu_+ = 0.01 \) (which may correspond to, say, \( c_0 = 1mM \) with \( a_+ = 2nm \) and \( a_- = 4.3nm \)) and (b) \( \nu_- = 10^{-3} \) and \( \nu_+ = 10^{-4} \) (corresponding to \( c_0 = 1mM \) with \( a_+ = 4.3A \) and \( a_- = 9.3A \)). As the negative ions are larger, they invade more surface and cause slip in the opposite direction to the electric field. This propels the particle in the same direction with the electric field, causing positive mobility even for a negatively charged particle.

Comparing the two plots in Fig.6-13, we can say that, as we approach the dilute limit, the particle mobility follows the PB theory and declines for a wider voltage range. Also, the initial charge of the particle does not matter as much at large voltages, when the electrolyte asymmetry eventually starts to affect the mobility. In addition, the mobility is eventually larger in less concentrated solutions at high enough voltages. At low concentrations (or for smaller ions with the same size ratio), the maximum MHS slip is larger for both ion types, and therefore more slip contribution is coming from the equatorial region. However, since the ratio of ion sizes is the same, the difference in the maximum MHS slip for the two types of ions remain the same. Therefore, the nonlinear capacitance effect grows with decreasing concentration, while the slip saturation effect stays the same. Therefore the extent to which the MHS slip theory reduces the effect of the asymmetric capacitances is lower, causing the stronger effects from the asymmetry of the electrolyte.

Electrophoretic motion of a particle is usually taken to be proof of nonzero total charge. This is indeed the case for non-polarizable particles. For polarizable particles, it has been shown that particle motion can result from asymmetric shapes. Our models show that, even

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Figure 6-13: Mobility of neutral and charged particles in an asymmetric electrolyte with (a) \( \nu_- = 0.1 \) and \( \nu_+ = 0.01 \) (b) \( \nu_- = 10^{-3} \) and \( \nu_+ = 10^{-4} \), reanalyzed with MHS theory (solid curves), in addition to the HS theory (dashed curves).

if the particle is symmetric and neutral, it may go under electrophoretic motion because of broken symmetries in the electrolyte. Conversely, a charged particle may stand still because of similar effects. Thus, unless the electrolyte is also symmetric, the electrophoretic mobility of a symmetric polarizable particle is not a reliable measure of (even the sign of) its total charge.
Chapter 7

Conclusions

There is a vast literature on the classical theory of electrochemical transport based on the dilute solution theory. All these works point out the many complex phenomena: surface transport of ions, Faradaic charging, bulk diffusion, and space charge. In this thesis, we challenge the starting point of the dilute solution theory, that is the treatment of the ions as mathematical points. We argue that it is not always appropriate to use this model. This is not to say that the standard theory is not a successful one, which it is, but only at low concentrations and low applied voltages. In fact, we use the low-voltage theory in chapter 3 to investigate the interaction of Janus particles with a planar boundary.

The main idea is the following: For an electrolyte solution to remain dilute everywhere, it not only needs to have low bulk concentration but also it cannot be exposed to large electric fields, which may squeeze its ions into thin regions where the solution is no longer dilute. In that case, finite size effects become important, and the problems solved with the dilute solution theory need to be revisited. In general, those size effects understandably lower the salt uptake into the double layers, thus reducing the extent of unusual phenomena such as concentration gradients and space charge.

It is a challenge to take finite size effects into account accurately in a mathematical model. In chapters 4 and 5, we proposed a basic model, derived from a lattice-gas approximation, originally due to Bikerman [21]. This simple model also helps us understand the limits of the dilute solution theory in quantitative terms. There are more accurate theories for finite size effects, based on the modeling of ions and the solvent as hard spheres, which is not a good approximation for aqueous solutions. Also, in the double layer, the ions are packed very closely, so the assumptions of the hard-sphere theories break down. In addition, the thickness of the double layer is usually less than a few ions, which makes the mean-field approximation questionable. The surface roughness and adsorption also need to be taken into account carefully for many metal electrode materials. It is perhaps because of all these difficulties that to our knowledge nobody has previously attempted to develop a steric theory of electrokinetics.

In this thesis, we have taken a first step towards that goal, which has helped us explain some of the puzzling experimental observations qualitatively. The theory helps us gain a deeper understanding of the double layer effects, although a quantitative agreement is still missing with ACEO experiments. This might be because of the inaccuracies in the description of finite size effects, or the failure of the (HS) electrokinetic slip formulae. In order to answer this question, more experiments are needed to gain understanding of these two phenomena. In particular, it
is essential to independently measure the two quantities (i) the surface differential capacitance (for the type of electrodes used in ACEO), and (ii) electrokinetic slip coefficient as a function of surface charge (especially for large surface charges).

The question "what are the Maxwell equations for electrokinetics?" remains unanswered, yet we are glad to have pointed out what the possible answer may look like, and when we might not need the full answer.
Appendix A

Double Layer Structure with Variable $\varepsilon(E)$

A.1 Introduction

In this section, we work out the general solution for the capacitance for any MPB equation with variable permittivity. For a simple one-dimensional setting, the Poisson Equation reads

$$- \frac{\partial}{\partial x} \left( \varepsilon \frac{\partial \psi}{\partial x} \right) = \rho$$  \hspace{1cm} (A.1)

In the electrochemical setting, the charge density $\rho$ is a function of $\psi$. We also assume that the permittivity $\varepsilon$ is a function of the electric field $E$, as formulated in the earlier work of Lyklema and Overbeek [117]. After multiplying by $E = -\frac{\partial \psi}{\partial x}$, the Poisson equation (A.1) takes the form

$$\rho(\psi) \frac{\partial \psi}{\partial x} = \frac{\partial}{\partial x} [\varepsilon(E)E] E$$

$$= [\varepsilon'(E)E^2 + \varepsilon(E)E] \frac{\partial E}{\partial x} \equiv h(E) \frac{\partial E}{\partial x}$$

where we define the function $h = h(E)$. Now, we can integrate both sides from the bulk ($\psi = 0$, $E = 0$) to the inside of the double layer ($\psi = \Psi_D$, $E = E_D$) to yield

$$p(\Psi_D) = H(E_D), \text{ or } E_D = H^{-1}(p(\Psi_D))$$  \hspace{1cm} (A.2)

with the functions

$$p(\Psi_D) = - \int_{0}^{\Psi_D} \rho(\psi) d\psi,$$ \hspace{1cm} (A.3)

$$H(E_D) = \int_{0}^{E_D} h(E) dE = \frac{1}{2} \varepsilon(E_D) E_D^2 + \frac{1}{2} \int_{0}^{E_D} \varepsilon'(E) E^2 dE$$

Note that the functions $p$ and $H$ are always positive, so there are an even number of solutions to the equation (A.2), unless $E_D = 0 = \Psi_D$. We could have avoided this by multiplying (A.1) with $|E|$ instead of $E$, with the cost of more complex algebra. For now, we will use the
information that

\[ \text{sign}(E_D) = \text{sign}(\Psi_D) \]

to choose the correct solution. In the following paragraphs, we will implicitly assume that \( E_D, \Psi_D > 0 \), with having in mind that the case \( E_D, \Psi_D < 0 \) is totally symmetric.

For the equation (A.2) to be uniquely solvable, the function \( H(E_D) \) need to be monotonically increasing to infinity as a function of the electric field. This is because \( p \) is not bounded from above, as its integrand \( \rho \) neither changes sign (except at the origin) nor approaches zero as \( \psi \to \pm \infty \). This constraint on \( H \) is the same as requiring that \( q = q(E_D) \) decreases (increases in absolute value, because signs of \( E_D \) and \( q \) are always opposite) as a function of the electric field \( E_D \) inside the double layer, as

\[
0 < \frac{d}{dE_D} (\log q) = \frac{d}{dE_D} (\log \varepsilon(E_D)E_D) = \frac{\varepsilon'}{\varepsilon} + \frac{1}{E_D}
\]

which implies that the derivative of \( H \),

\[
\frac{dH}{dE} = h(E) = \varepsilon E^2 \left( \frac{\varepsilon'}{\varepsilon} + \frac{1}{E} \right)
\]

is positive for all \( E > 0 \) (and negative for \( E < 0 \)). In general, the requirement is that

\[
h_2(E) \equiv \frac{h(E)}{E} = \varepsilon'E + \varepsilon
\]

be positive for all \( E \).

### A.2 Examples of possible \( \varepsilon(E) \)

According to Bockris and Reddy ([24], e.g. see Fig.6-94 on page 899), the dielectric constant \( \varepsilon_r = \frac{\varepsilon}{\varepsilon_0} \) drops from a value of around 78 in the bulk to around 6 at the charged electrode surface.

1) A functional form that satisfies such a profile is given by

\[
\varepsilon(E) = \varepsilon_i + \frac{\varepsilon_b - \varepsilon_i}{1 + \left( \frac{E}{E_s} \right)^2}
\]

with \( \varepsilon_b = 78\varepsilon_0 \) and \( \varepsilon_i = 6\varepsilon_0 \). A simple calculation yields

\[
H(E) = \frac{1}{2}\varepsilon_i E^2 - (\varepsilon_b - \varepsilon_i) \left[ \frac{1}{2} E_s^2 \ln[1 + \left( \frac{E}{E_s} \right)^2] - \frac{E^2}{1 + \left( \frac{E}{E_s} \right)^2} \right]
\]

which may or may not be monotonically increasing, depending on \( E_s \). For unique solutions to (A.2), we need \( h_2(E) = \varepsilon'E + \varepsilon \geq 0 \) for all \( E \). Solving for \( h_2'(E) = 0 \) yields \( E = \sqrt{3}E_s \), where \( h_2 \) attains a potentially negative local minimum

\[
h_2(\sqrt{3}E_s) = \varepsilon_i - \frac{(\varepsilon_b - \varepsilon_i)}{8}
\]
which is negative for the values $\varepsilon_b = 78\varepsilon_0$ and $\varepsilon_i = 6\varepsilon_0$, regardless of $E_0$. We will not be using (A.4) for this reason.

2) The functional form for $\varepsilon$ in (1) declines too quickly from $\varepsilon_b$ to $\varepsilon_i$, almost suddenly as the electric field gets bigger compared to the scale $E_0$. We can propose the more general form

$$\varepsilon(E) = \varepsilon_i + \frac{\varepsilon_b - \varepsilon_i}{(1 + (\frac{E}{E_0})^2)^{\alpha}}$$

(A.5)

Here we take $\alpha = \frac{1}{2}$, which allows for a lot of analytical progress. In this model, $h_2(E) = \varepsilon_i + \frac{(\varepsilon_b - \varepsilon_i)}{(1 + (\frac{E}{E_0})^2)^{3/2}}$, which is clearly positive for all $E$. Integrating $h(E) = h_2(E)E$, we obtain

$$H(E) = \frac{1}{2}\varepsilon_i E^2 + (\varepsilon_b - \varepsilon_i) E_0^2 \left[1 - \frac{1}{\sqrt{1 + (\frac{E}{E_0})^2}}\right]$$

A.3 Double Layer Capacitance

Now, we turn back to our main goal and calculate the differential capacitance of the double layer under this model of $E$--dependent permittivity. The double layer charge density is given by

$$q = -\varepsilon(E)E|_{\psi = \Psi_D} = -\varepsilon(E_D)E_D$$

Therefore the capacitance is-

$$C(\Psi_D) = -\frac{dq|_{\psi = \Psi_D}}{d\psi} = [\varepsilon'(E_D)E_D + \varepsilon(E_D)] \frac{dE}{d\psi}(\Psi_D)$$

$$= [\varepsilon'(E_D)E_D + \varepsilon(E_D)] \frac{-\rho(\Psi_D)}{h(E_D)} = \frac{-\rho(\Psi_D)}{E_D}$$

Note that, if $\varepsilon = \varepsilon_b$ is constant, then $E_D = \frac{-\partial\psi|_{\psi = \Psi_D}}{\partial x} = -q_0(\Psi_D)/\varepsilon_b$ and we recover the standard formula:

$$C_0(\Psi_D) = \varepsilon_b \frac{\rho(\Psi_D)}{q_0(\Psi_D)}$$

The effect of an electric-field dependent $\varepsilon = \varepsilon(E)$ (instead of constant $\varepsilon = \varepsilon_0$) on the capacitance is measured by the function

$$\frac{C(\Psi_D)}{C_0(\Psi_D)} = \frac{E_0(\Psi_D)}{E(\Psi_D)} = \frac{E_0(\Psi_D)}{H^{-1}(\rho(\Psi_D))} \equiv F(\Psi_D)$$

where

$$E_0(\Psi_D) = \sqrt{-\frac{2}{\varepsilon_b} \int_0^{\Psi_D} \rho(\psi) d\psi} = \sqrt{\frac{2\rho}{\varepsilon_b}}$$
For the PB model, we have

\[ \rho = -\sinh \psi, \quad p(\Psi_D) = \cosh \Psi_D - 1, \]

\[ E_0(\Psi_D) = \frac{2}{\sqrt{\varepsilon_0}} \sinh \frac{\Psi_D}{2} \]

\[ C_0(\Psi_D) = \cosh(\Psi_D/2) \]

and for the MPB, we have

\[ \rho = \frac{\sinh \psi}{1 + \nu (\cosh \psi - 1)}, \quad p(\Psi_D) = \frac{1}{\nu} \ln \left[ 1 + \nu (\cosh \Psi_D - 1) \right] \]

\[ E_0(\Psi_D) = \frac{1}{\sqrt{\varepsilon_0 \nu}} \sqrt{\ln(1 + \nu (\cosh \Psi_D - 1))} \]

\[ C_0(\Psi_D) = \frac{\sinh(\Psi_D)}{1 + \nu (\cosh \Psi_D - 1)} \frac{1}{\sqrt{\nu \ln(1 + \nu (\cosh \Psi_D - 1))}} \]

For plotting purposes, all the quantities can be expressed as a function of the variable \( E \), and plotted. Namely, we can use the equality

\[ \Psi_D(E) = \cosh^{-1} (1 + H(E)) \]

in the PB theory, and

\[ \Psi_D(E) = \cosh^{-1} \left( \frac{e^{\nu H(E)} - 1}{\nu} + 1 \right) \]

in the MPB theory.

**A.4 Conclusions**

The decrease of permittivity in the double layer causes a decline in the differential capacitances, in both the PB and MPB models. In the PB model, the exponential behaviour of the capacitance is not totally eliminated, but postponed to higher applied voltages. In the MPB theory, the capacitance peaks at a smaller maximum and starts to decline at smaller voltages. This may help us partly explain why such big effective ion sizes \( a \) need to be taken in the MPB theory to obtain reasonable results. If taken into account, it may thus lower the values for \( a \), and make them more realistic.

The permittivity dependence on the electric field surely affects the electrokinetic slip at the surface, too. If we assume that the viscosity is constant -which it is not-, then the electrokinetic slip depends on the voltage-averaged permittivity through according to the HS slip formula (6.14). As the concentration increases, there is more buildup in the condensed layer and a large potential drop is realized over a thicker double layer. Thus, at large applied voltages, the electric field is reduced in the double layer. This means an increase in the permittivity and the electrokinetic slip, with increasing concentration. This contradicts the experimental data, but it also proves that the effect of induced viscosity increase is the more dominant effect, as argued in [114].

Also, we cannot obtain a full flow saturation through decreasing permittivity, as it always has
a lower bound $\varepsilon_i > \varepsilon_0$. We have not delved into detail in electrokinetics implications of variable $\varepsilon$ in this section, because one must consider the change in viscosity $\eta$ in the double layer in the analysis of electrokinetic slip.
Appendix B

Derivation of the Steric Entropy

The simplest derivation for Bikerman's formula can be found in [26], a shorter version of which we repeat here for completeness. Imagine that the domain of interest is divided into a large number of infinitesimal cells. Suppose that those cells, albeit infinitely small, still contain a large number, $N$, of lattice sites, each holding an ion or a solvent molecule. For a certain volume cell $\Delta V$, the canonical partition function is

$$Q = \exp\left(-\frac{W_{c}}{kT}\right) \frac{N!}{n_{+}! n_{-}! (N - n_{+} - n_{-})!} \quad (B.1)$$

where $n_{\pm}$ is the number of $\pm$ ions in the volume cell, which have an electrostatic energy density of $W_c$. In the mean field theory, this energy density is simply given by

$$\Delta W_c = \frac{1}{2} \epsilon |\nabla \psi|^2 \Delta V$$

where $\psi$ is the electrostatic potential achieved in $\Delta V$. The free energy of the solution in this cell can be obtained from the statistical mechanical relation

$$\Delta F = -kT \ln(Q)$$

$$= \Delta W_c + \ln n_{+}! + \ln n_{-}! + \ln(N - n_{+} - n_{-})! - \ln N!$$

Using the Stirling’s approximation, we can approximate this quantity by

$$\Delta F = \frac{1}{2} \epsilon |\nabla \psi|^2 \Delta V + kT(n_{+} \ln \frac{n_{+}}{N} + n_{-} \ln \frac{n_{-}}{N}$$

$$+ (N - n_{+} - n_{-}) \ln \left(\frac{N - n_{+} - n_{-}}{N}\right)) \quad (B.2)$$

If the effective size for ion species and the solvent is $a$, we can write this last expression as

$$\Delta F = \frac{1}{2} \epsilon |\nabla \psi|^2 \Delta V + kT \Delta V [c_{+} \ln c_{+}a^3 + c_{-} \ln c_{-}a^3$$

$$+ \frac{(1 - c_{+}a^3 - c_{-}a^3)}{a^3} \ln(1 - c_{+}a^3 - c_{-}a^3)]$$

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by using the relation $n_\pm = c_\pm \Delta V = c_\pm N a^3$. Therefore, the free energy density is

$$F = \frac{\Delta F}{\Delta V} = \frac{1}{2} \varepsilon |\nabla \psi|^2 + \frac{kT}{a^3} [c_+ a^3 \ln c_+ a^3 + c_- a^3 \ln c_- a^3 + (1 - c_+ a^3 - c_- a^3) \ln (1 - c_+ a^3 - c_- a^3)]$$

(B.3)

The assumption that the ion species and the solvent molecules all have the same size may not be accurate in most situations. This is because the ions are solvated, therefore occupy much larger volume than the solvent. In addition, the interaction of the ions with each other and the solvent may vary in strength and nature. Still, the same size assumption is essential in the above derivation to get a simple formula such as (B.3). In order to account for different sizes, the more accurate BMCSL formula can be employed (see the section on "More Accurate Theories of Finite Size Effects").
Appendix C

Asymmetric Electrolytes

For asymmetric electrolytes, the derivation in the previous section is valid until the equation (B.2), where we can no longer put in the relation \( n_\pm = c_\pm \Delta V = c_\pm N a^3 \), which is replaced by

\[
\begin{align*}
  n_\pm &= c_\pm \Delta V \\
  N &= (c_- + c_+ + c_w) \Delta V
\end{align*}
\]

where

\[ c_w = \frac{1}{a_w^3} (1 - c_+ a_+^3 - c_- a_-^3) \tag{C.1} \]

is the concentration of the solvent molecules. Carrying on the algebra, we arrive at

\[
F = \frac{1}{2} \varepsilon |\nabla \psi|^2 + kT[c_+ \ln (c_+) + c_- \ln (c_-) + c_w \ln (c_w) + \ln (c_+ + c_- + c_w)]
\]

where only the two concentrations are independent variables, and \( c_w \) is given by (C.1). Note that the additional last term in (C.2) would just be a constant in case of equal sizes for all species. The chemical potentials are calculated to be

\[
\mu_\pm = z e \psi + kT[\ln \frac{c_\pm}{c_+ + c_- + c_w} - \frac{a_\pm^3}{a_w^3} \ln \frac{c_w}{c_+ + c_- + c_w}]
\]

The numerically computed differential capacitance is plotted in the Fig.C-1 for the case \( a_+ = 3A, a_- = 6A, a_w = 3A \) at a concentration \( c_0 = 10mM \), along with the symmetrical cases \( a_{\pm, w} = 3A \) and \( a_\pm = 6A, a_w = 3A \) at the same bulk concentration. The asymmetric capacitance picks up the positive arm from the \( a_{\pm, w} = 3A \) curve, and the negative arm from the \( a_\pm = 6A \) curve. This is expected, and it provides grounds for the model of the equation (6.13).

The \( \nu_{\pm} \) - model (6.13) is quite successful, because at small potentials the size effects do not matter anyway, and at larger potentials practically only one type of ions are in the double layer. The co-ion concentrations decrease exponentially, if not faster. However, there are also be solvent molecules in the double layer, whose concentration does not decay so fast at large voltages. Their size is assumed to be the same as those of the counter-ions in the simple \( \nu_{\pm} \) -
model.

We investigate the effect of the size of the solvent molecules on the differential capacitance in Fig.C-2 for a symmetric electrolyte of sizes $a_{\pm} = 6\text{A}$ and bulk concentration $c_0 = 10mM$. The solid curve shows the equal-sizes case, $a_w = 6\text{A}$, and corresponds to the simple symmetric MPB model. When the solvent molecules have smaller sizes, like $a_w = 1\text{A}$ of the dashed curve, the capacitance is lower because it is harder to expel them completely from the double layer at moderate voltages. Conversely, having large solvent particles facilitates the forming of a condensed layer full of only counterions, and increases the differential capacitance, as shown by the dotted curve for $a_w = 9\text{A}$. Nevertheless, the overall differential capacitance is hardly affected by the solvent size. All three curves shown in Fig.C-2 agree at small ($\Psi_D < 3\frac{kT}{ze}$) as well as large ($\Psi_D > 10\frac{kT}{ze}$) potentials. This is yet another justification for the use of the simple $\nu_{\pm}$- model for asymmetric electrolytes.

Figure C-3 attempts to fit the experimental capacitance of silver electrodes in NaF solution obtained by [191]. The capacitance data is clearly not symmetrical with respect to the Na and F ions. On the negative side of the point of zero charge (p.z.c.), the capacitance peaks earlier and starts to decrease, corresponding to Na ions, while to the right of p.z.c., the capacitance has a larger peak, whose value increases with the bulk concentration. Choosing different sizes for the two ions, the MPB model yields two different curves on the two sides of the p.z.c., however, it predicts that the peak values for the Flour ion is independent of the bulk concentration. To predict the peak variation, we may need to allow the ion size to depend on the electric field: $a_- = a_-(E)$. At higher concentrations, there is larger electric field in the diffuse layer and this may justify the smaller ion sizes, which would yield a larger peak value in the differential capacitance. Also, note that the capacitance decay in the MPB theory is not sharp enough after the peak occurs.
Figure C-2: Differential capacitances with effective ion sizes $a_\pm = 6A$, and varying effective solvent sizes $a_w = 1A, 6A$ and $9A$.

Figure C-3: Experimental capacitance of a silver electrode in NaF solution [191] matched with MPB capacitance: $C_S = 200\mu F/cm^2$, $a_- = 8A$, $a_+ = 13A$. 
Appendix D

Ionic Liquid Limit of Steric Model

A liquid that contains only ions and no solvent, and has a relatively low melting point (below 100°C) is called an ionic liquid. Some examples are 1-methylimidazole (used to recover acids from an existing process) and 1-butyl-3-methylimidazolium tetrafluoroborate ($BMIM - BF_4$). Typically, the ionic liquid contains a large organic fattyion ($BIMM$), and a much smaller alkaline or halide ($BF_4$).

Ionic liquids are more durable to oxidation and reduction at larger voltages, and thus have potential to replace the aqueous electrolytic solutions in supercapacitors. This makes the understanding of the ionic liquid-metal interface and its differential capacitance an important task. In this section, we analyze the MPB models in the limit of $\nu = 1$, which correspond to the vanishing of the solvent concentration. Would this yield any useful information about the ionic liquids? Due to the lack of extensive theoretical work and experimental work, we cannot give a definite answer, but, it might, according to [102], who argues that one may even take $\nu < 1$ to model them, indicating there may be room for compression under a large electric field.

In this section, we start with a re-derivation of the MPB theory in the absence of solvent, and plot the capacitances for various large values of $\nu$. Because ionic liquids generally have ions with very different sizes, we consider the case of asymmetric MPB theory in somewhat further depth than before. We find that the asymmetric ion sizes can lead to a shift in the differential capacitance curves. This might be an explanation for why the point of zero charge measurements from an electrocapillary maximum does not give the minimum of the differential capacitance measured using impedance methods. Finally, we finish the section by repeating our analysis for slightly smaller $\nu$ values, when the ionic liquid has some void lattice in it.

When the effective ion sizes are both equal to $a$, the only two species fill up the space, we have $c_+a_+^3 + c_-a_-^3 = 1$, from which we can express

$$c_+ = \frac{1}{a_+^3}(1 - c_\pm a_\pm^3) \quad (D.1)$$

Therefore, the concentration of only one species, say $c_+$, is enough to describe an ionic liquid. The internal energy is

$$U = \int dr \left( -\frac{\varepsilon}{2} |\nabla \psi|^2 + ze\psi(c_+ - c_-) \right)$$
and the entropic contribution to the free energy is

$$-TS = kT \int dr \left[ c_+ \ln c_+ + c_- \ln c_- - (c_+ + c_-) \ln(c_+ + c_-) \right]$$

Then the chemical potential is given by

$$\mu_+ = \frac{\delta F}{\delta c_+} = ze(1 + \frac{a_+^3}{a_-^3}) \psi + kT \left[ \ln \frac{c_+}{c_+ + c_-} - \frac{a_+^3}{a_-^3} \ln \frac{c_-}{c_+ + c_-} \right]$$

$$= ze(1 + \alpha_+) \psi + kT [\alpha_+ \ln(1 + r_+) - \ln(1 + \frac{1}{r_+})]$$

with the notation $\alpha_+ = \frac{a_+^3}{a_-^3}$ and $r_+ = \frac{c_+}{c_-}$. In order to obtain concentrations at equilibrium (i.e. $\mu_+ = \text{constant}$), one needs to solve the equation

$$r_+ \left( \frac{1 + r_+}{2} \right)^{\alpha_+ - 1} = e^{-kT \psi(1 + \alpha_+)}$$

(D.3)

numerically, unless $\alpha_+$ takes on few of the special values. Then, the concentrations are given by

$$c_+ = \frac{1}{\alpha_+ + r_+}$$

and (D.1). After obtaining the function $c_+ (\psi)$, we integrate $\rho = c_+(1 + \alpha_+) - 1/a_3$ to obtain $q = \sqrt{-2 \int_0^{\Phi(\rho)} \rho d\psi}$, and finally differentiate $q$ to get the differential capacitance $C$.

For equal ion sizes $a_+ = a_- = a$, and $\alpha_+ = 1$, the steady solution is given by

$$c_+ a_3 = \frac{e^{-ze\psi/kT}}{2 \cosh(ze\psi/kT)}$$

The modified ionic liquid equations are

$$\frac{\partial c_+}{\partial t} = 2zeb \nabla \cdot (c_+ \nabla \psi) + D \nabla^2 c_+ - D \nabla \cdot \left( \frac{c_+ a_3^2}{1 - c_+ a_3^3} \nabla c_+ \right)$$

where the last term represents a reduction in the diffusion due to finite size effects. As before, we can calculate the charge in the double layer,

$$q = \sqrt{\frac{2ekT}{a_3^3} \ln \cosh(\frac{ze \xi}{kT})} = \frac{ze}{a_3^3} \lambda D \sqrt{2 \ln \cosh(\frac{ze \xi}{kT})}$$
Figure D-1: Differential capacitance of ionic liquids in the MPB theory, with the ion size ratios $\alpha_+ = \left(\frac{a_+}{a_-}\right)^3 = 1, 3, 8$ and $1/8$.

The capacitance maximum at zero voltage is contradictory with some of the experimental work [75] on molten salts, however the shift of the point of zero charge is consistent with the findings of [130] on ionic liquids. Recently, molecular dynamic simulations [59] have yielded similar results to the ones reported here.
Appendix E

Alternative Theories of Finite Size Effects

There have been attempts to calculate the chemical potential for a mixture of hard-spheres. For equal sized spheres, the Carnahan-Sterling formula [36] states that the excess chemical potential is

\[ \mu_i^{ex} = \frac{\phi(8 - 9\phi + 3\phi^2)}{(1 - \phi)^3} \]  

(E.1)

For spheres of different sizes, this is generalized to the Boublik-Mansouri-Carnahan-Starling-Leland (BMCSL)[37, 121] formula

\[
\mu_i^{ex} = -\left(1 + \frac{2\xi_3^3 a_i^3}{\phi^3} - \frac{3\xi_2^2 a_i^2}{\phi^2}\right) \ln(1 - \phi) + \frac{3\xi_2 a_i + 3\xi_1 a_i^2 + \xi_0 a_i^3}{1 - \phi} \\
+ \frac{3\xi_2 a_i^2}{(1 - \phi)^2} \left(\frac{\xi_2}{\phi} + \xi_1 a_i\right) - \frac{\xi_3^3 a_i^3 \phi^2 - 5\phi + 2}{\phi^2(1 - \phi)^3} 
\]

(E.2)

where \( a_i \) is the diameter of the ion type \( i \), \( \xi_\alpha = \sum_j c_j a_j^\alpha \), and \( \phi = \xi_3 \) is the volume fraction of ions. Only the ionic species are considered in the formulae (E.1) and (E.2), but "spherical" solvent particles could be added, although this may not be a good idea because of the polar nature and non-spherical geometry of water molecules. Another visible shortcoming of the BMCSL chemical potential is its divergence at the volume fraction \( \phi = 1 \), which cannot be achieved by hard spheres even at close packing. Although complicated, the formula (E.2) remains to be an analytical expression, therefore very simple compared to any DFT studies or molecular dynamics simulations.

It was Lue et al. [112] that proposed the use of the CS and BMCSL in the analysis analyze electrolyte solutions, then diCaprio et al.[49] utilized the CS formula to analyze the double layer structure. Recently, Biesheuvel and Soestbergen [18] analyzed the case when there are two different type of counterions in the double layer. They found out that ions compete to be closer to the electrode. At high charge densities, the smallest ions (ions carrying most charge per volume) form a diffuse layer of their own by the electrode surface, pushing out the larger ions to a second diffuse layer.
E.1 Comparison of CS and MPB Models

While CS excess chemical potential (E.1) diverges at $\phi = 1$, this is hardly realized in electrochemical potentials. The chemical potential (E.1) increases much more rapidly than its Bikerman (MPB) counterpart

$$\mu_i^{ex} = -\ln(1 - \phi)$$

which is dormant until $\phi$ gets really close to the full volume fraction. This is illustrated in Fig.E-1, where the counterion volume fractions at the surface are plotted as a function of the double layer voltage drop. The bulk concentration is taken to be $c_0 = 10mM$ and the effective ion size is $a = 6A$ for both models. The MPB model quickly reaches maximum concentration at moderate voltages, whereas the CS model predicts a maximum volume fraction of $\%21$ even at $1000kT/ze$. This shows that the finite size effects are underestimated by the MPB model.

The counterion concentrations near the surface in the CS model is shown in Fig.E-2(a) for the same electrolyte, at double layer potentials $\Psi_D = 5, 10, 20, 40, 60, 80$ and $100kT/ze$. Note that the diffuse layer extends much further into the electrolyte, few tens of Debye lengths compared to one or two Debye lengths in the MPB theory, shown in Fig.E-2(b). The lower concentrations, as well as a larger diffuse layer predicted by the CS theory are both good news for the mean-field theory.

The differential capacitance in the two models, CS and MPB, are compared in Fig.E-3. In order to make up for the MPBs underestimation of steric effects, the $\nu$ values are multiplied by an extra factor of 5, so that $\nu_{MPB} = 10c_0a^3 (= \frac{30}{\pi} \phi_{bulk})$. This helps the two differential capacitances agree in the tails, because the maximum concentrations are about equal at large voltages (recall that CS theory predicts $\%20$ volume fraction at large voltages). Even with this enhancement of $\nu_{MPB}$, the MPB theory still underestimates the size effects and predicts larger differential capacitances. Specifically, at several times the thermal voltage $\frac{kT}{ze}$, the MPB capacitance is still much larger than its CS counterpart. In the case of $c_0 = 1mM$, the plotted
Figure E-2: Diffuse layer counterion concentrations in the (a) CS theory, (b) MPB theory, at voltages $\Psi_D = 5, 10, 20, 40, 60, 80, 100 \frac{KT}{ze}$. The bulk concentration is $c_0 = 10mM$, and the effective ion size (diameter) is $a = 6A$, in both plots. The figure (b) also shows the PB counterion density (dash-dot), which remains virtually unchanged for $\Psi_D > 10 \frac{KT}{ze}$.

Figure E-3: Differential Capacitance curves for the CS theory and the simple MPB. The bulk concentrations are $c_0 = 1$ (not labeled), 10 and 100mM. The effective ion size is $a = 6A$. For the MPB model, $\nu$ is taken to be 5 times its corresponding value ($2c_0a^3$).
Figure E-4: Differential capacitances at various ion concentrations in (a) CS theory with ion diameter $a = 4\text{A}$ (b) MPB theory with effective ion size $a = 12\text{A}$.

curves (the bottom-most ones in Fig.E-3) show that the CS capacitance has a maximum at zero while the MPB still predicts a minimum there.

Neither the CS nor the MPB model is the final answer in the theory of electrolytes. We have used the MPB theory in most of this thesis, because we became aware of the CS theory much later. The examples in this section somewhat justify our taking unrealistically large $\nu$ values in the earlier chapters of the thesis. Add to this the reduced permittivity in the double layer, and the effective size of ions in the MPB theory can easily be taken at least twice as much as they are.

E.2 Comparison with Experimental Capacitances

In general, it is hard to make a direct comparison with experimental data because of the specific adsorption to the electrode surface. For this reason, we will focus on the data of [191, 192] for silver electrodes which present minimal specific adsorption. Qualitatively, both the CS and the MPB models can produce the main features of the experimental differential capacitances, which are: (i) nonmonotonic differential capacitance, in other words, the capacitance first increases, then decreases as one moves away from the capacitance minimum at the supposed point of zero charge (ii) the capacitance minimum increases with increasing concentration, and (iii) at large voltages, the differential capacitance is independent of concentration. In order to get these results, one has to take large numbers for the ion diameters (which we call the effective ion sizes) in both steric theories. The figures show the capacitances, which look terribly like the Fig.3 of [191] and [192].

DiCaprio et al. [49] has already pointed out the qualitative success of the CS theory, however no quantitative matchings were reported by them, who were content by the statement "a quantitative comparison with the experimental results is not possible at this stage". In
Figure E-5: Differential capacitance data in Fig.3 of [191] is fitted by (a) CS model (b) the MPB model. The effective ion diameter is taken to be $a = 4A$ for the CS model, whereas the size of ions is $a = 11A$ for the MPB model.

In fact, there is good reason for their silence, as the CS theory fails to predict the sharp drop of differential capacitance at moderate voltages. This is shown in Fig.E-4(a), where we fit the data of Fig.3. in [191] for $KPF_6$ with the CS theory. The best match is obtained with the ion diameter $a = 4A$ and the Stern capacitance $C_{stern} = 125\mu F/cm^2$. In addition, the capacitance is multiplied by the surface roughness $R = 1.1$, value taken from G. Valette[191]. Unlike him, we assume that the roughness is constant for all concentrations, which results in a poor fit for $c_0 = 100mM$ (which could be improved by readjusting the Stern capacitance and the ion diameter as well). In general, the model compares well with the data in the central region but it cannot reproduce the capacitance drop at the wings.

Although not perfect, the MPB theory, albeit with much larger effective ion sizes, does a better job in capturing the shape of the capacitance curve. For the matching shown in Fig.E-4(b), the fitting parameters are the same as before except for the effective ion size $a = 11A$. The biggest improvement takes place in the moderate to large voltage regime, when the differential capacitance drop is predicted well by the MPB theory.

This little study on the experimental data does not imply that the MPB model is superior to the CS theory, because, among many other things, we have left out the effect of the drop in the dielectric constant due to the electric fields in the diffuse layer. This effect may reduce the differential capacitance at moderate voltages, and help the CS theory fit the data better. More analysis is needed on the one-to-one comparison of the steric models with the data for a deeper understanding of the electrode/electrolyte interface.
Appendix F

Effects of Specific Adsorption

Most of this thesis deals with the diffuse part of the double layer. In this section, we briefly address the adsorption phenomena at the surface and attempt to integrate it with our steric models. Ions in the solution can adsorb the surface with reaction

\[ \text{Ion(solution)} + \text{Site(EMPTY)} \rightleftharpoons \text{Ion(adsorbed)} + \text{Site(occupied)} \quad (F.1) \]

The inner Helmholtz plane (IHP) corresponds to the locus of the adsorbed ions, and its distance from the metal, \( \lambda_a \), is approximately half an ion diameter. The solvated ions in the solution cannot get closer to the IHP by a certain distance \( \lambda_a \) which corresponds the outer Helmholtz plane (OHP). This length, \( \lambda_s \), is about the sum of the radius of an adsorbed ion and the solvation shell\(^1\).

We assume the charge of an adsorbed ion is concentrated at the IHP plane, \( x = \lambda_a \), so both the inner and the outer compact layers are charge free. The potential therefore follows a linear profile in those regions, albeit with a slope change at the IHP plane because of the charge there and the possible difference in the inner and outer layers permittivities \( \varepsilon_i \) and \( \varepsilon_s \). The model is summarized in Fig.F-1.

The adsorbed ion concentration at the IHP is given by an equilibrium relation

\[ c_{\pm}^a = f(c_{\pm}(0), \Delta \phi_a) \]

where \( c_{\pm}(0) \) are the bulk concentrations of ions and \( \Delta \phi_a \) the potential drop over the inner compact layer (i.e. surface/IHP layer). When the Langmuir isotherms are used, this relation becomes

\[ \frac{\theta_{\pm}}{1 - \theta_{\pm}} = k_a \exp \left( \mp \frac{e \Delta \phi_a}{kT} \right) c_{\pm}(0) \quad (F.2) \]

where \( \theta_{\pm} = c_{\pm}^a a_s^2 \) is the surface coverage, and \( a_s \) is the effective size of adsorbed ions.

Electrostatic boundary conditions at the two interfaces \( x = \lambda_a \) and \( x = \lambda_a + \lambda_s \) are,

\(^1\)We use subscripts \( a \) and \( s \) for adsorption and solvation layers, instead of \( i \) and \( o \) for inner and outer layers, because \( i \) is usually used as an index and \( o \) resembles zero.
Figure F-1: The potential profile in the adsorption, solvation, and the diffuse layers.

respectively,

\[ 0 = -\varepsilon_b \frac{\partial \psi}{\partial x} - \varepsilon_a \frac{\Delta \psi_a}{\lambda_a} = -C_a \Delta \psi_a - q_d \]

\[ q_a = \varepsilon_a \frac{\Delta \psi_a}{\lambda_a} - \varepsilon_s \frac{\Delta \psi_s}{\lambda_s} = C_a \Delta \psi_a - C_s \Delta \psi_s = q_d - C_s \Delta \psi_s \]

where \( C_a = \frac{\varepsilon_a}{\lambda_a} \) and \( C_s = \frac{\varepsilon_a}{\lambda_s} \) are the unit capacitances of the inner and outer compact layers, \( q_a \) and \( q_d \) are the surface charge densities in the adsorption and diffuse layers. The total charge density is \( q = q_a + q_d \), and the total potential drop of the double layer is

\[ \Delta \psi = \Delta \psi_a + \Delta \psi_s + \Delta \psi_d \]

\[ = -\frac{q_d}{C_a} - \frac{q_d + q_a}{C_s} + \Delta \phi_d \]

We will calculate the differential capacitance from

\[ C = -\frac{dq}{d(\Delta \psi)} \]

In order to simplify the computations, we consider \( \Delta \phi_d \) to be the independent variable, from which we can easily compute \( q_d \). Then we only need \( q_a \) to calculate the capacitance, which will
come from the Langmuir isotherm in (F.2), as

\[
q_a = \frac{ze(\theta_+ - \theta_-)}{a_{a,+}^2 - a_{a,-}^2} = \frac{(ze/a_{a,+}^2)}{1 + (k_{a,+}c_+(0))^{-1}\exp\left(\frac{z\phi_a}{kT}\right)} - \frac{(ze/a_{a,-}^2)}{1 + (k_{a,-}c_-(0))^{-1}\exp\left(-\frac{z\phi_a}{kT}\right)}
\]

where \(a_{a,\pm}\) are the sizes of the adsorbed ions, and

\[
\Delta \phi_a = -\frac{q_d}{C_a}, \quad c_\pm(0) = c_\pm, m_{pb}(c_0, \Delta \phi_d)
\]

The functions \(c_\pm, m_{pb}(c_0, \Delta \phi_d)\) can be taken from any general steric theory, such as the BMCSL or the simple MPB of chapters 4 and 5.

As an example, the specific adsorption model, along with the MPB, is fitted to the data of Grahame [74] in Fig.F-2 at bulk concentrations \(c_0 = 1, 10, 100\) and 916 mM of the electrolyte NaF. The parameters are \(a_{a,\pm} = 1\,A, a_- = 1.6\,nm, a_+ = 1.25\,nm, k_{a,+} = 2 \times 10^{-4}, k_{a,-} = 3 \times 10^{-5}, \epsilon_a = 4.6\epsilon_0, \epsilon_a = 40\epsilon_0\). The effective ion sizes are pretty large, and unrealistic for sodium fluoride, but realistic values can be used with CS model to obtain a similar fit to the data. While the fit for \(c_0 = 916\,mM\) is not very convincing, it captures something that the PB theory would not: the increase of capacitance in the low voltage region. Contrary the PB theory, the minimum of the differential capacitance at the p.z.c. turns into a maximum at high concentrations in the steric models. In the mercury data, specific adsorption jams the capacitance data and conceals this feature to some extent.

Note that at this high concentration, the parameter \(\nu > 1\), so we cannot legitimately use the MPB theory, unless we make \(a_\pm\) smaller. Still, we can treat the MPB formulae as mere analytical expressions without a theory, which we did in Fig..F-2 for \(c_0 = 916\,mM\) plot.
Figure F-2: Differential capacitance data from Grahame [74] for NaF at room temperature is fitted by the specific adsorption model using the MPB steric model. Note that all other parameters are kept constant for different bulk concentrations.
Bibliography


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