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ABSTRACT

A NUMERICAL METHOD FOR ELECTRO-KINETIC FLOW WITH
DEFORMABLE INTERFACES

by
Manman Ma

We consider two-phase flow of ionic fluids whose motion is driven by an imposed electric field. At a fluid-fluid interface, a screening cloud of ions develops and forms an electro-chemical double layer or ‘Debye layer’. The applied electric field acts on the ionic cloud it induces, resulting in a strong slip flow near the interface. This is known as ‘induced-charge electro-kinetic flow’, and is an important phenomenon in microfluidic applications and in the manipulation of biological cells. The models with two different cases including the fast or slow charging time scales are studied both analytically and numerically. We address a significant challenge in the numerical computation of such flows in the thin-double-layer limit, by using the slenderness of the layer to develop a fast and accurate ‘hybrid’ or multiscale numerical method. The method incorporates an asymptotic analysis of the electric potential and fluid dynamics in the Debye layer into a boundary integral numerical solution of the full moving boundary problem.

We present solutions for the quasi-steady state problem with $\Psi = O(1)$ and solutions for the time dependent problem with $\Psi \ll 1$, where $\Psi$ is the dimensionless surface potential. Leading order problems for both electric fields and fluid fields are solved with boundary conditions and matching methods. The small deformation theories when $Ca$ is small ($Ca$ is the electric capillary number) for both quasi-steady state and time dependent problems are developed to check numerical simulations.
A NUMERICAL METHOD FOR ELECTRO-KINETIC FLOW WITH DEFORMABLE INTERFACES

by

Manman Ma

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I dedicate this dissertation to my wonderful family.
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 CHAPTER 1

INTRODUCTION

Electrohydrodynamics, which is usually called EHD, deals with the fluid motion induced by DC or AC electric fields. When a drop is suspended in a fluid with an applied electric field, the discontinuity of the electric stress at the interface can cause deformation of the drop. There is a large literature on classical electrohydrodynamic phenomena, which concerns the behavior of drops and particles in conducting or dielectric fluids (a dielectric is an electrical insulator that can be polarized by an applied electric field). The earliest record of an electrohydrodynamic experiment is from the 17th century, describing the formation of a conical shape upon bringing a charged rod above a sessile drop (see, e.g., [1]). Most of the work on classical EHD up until the early 1960s focused on the behavior of fluids that are perfect conductors or perfect dielectrics. This began to change in the early 1960s with the first work on poorly conducting liquids [2]. In the mid 1960s, GI Taylor [3] introduced the leaky dielectric model to analyze the deformation of drops immersed in a poorly conducting fluid and acted on by an imposed DC field. The paper [4] reviewed the foundations of the leaky dielectric model and compared experiments with features of the model. Past investigations in classical EHD include numerical work that uses the boundary integral method to study the deformation of drops immersed in a viscous fluid and acted on by an imposed electric field. For example, [5, 6, 7, 8] studied the deformation and breakup of axisymmetric droplets in an electric field.

Another branch of EHD, electrokinetics, deals with the behavior of particles in aqueous electrolytes. Particles can be solid, liquid or gas bubbles. An electrolyte is any substance containing free ions that makes the substance electrically conductive. There is a major difference in the behavior of dielectric fluids and electrolytes that is
caused by electrokinetic phenomena. An electrolyte possesses free ions that can move when an electric field is applied. In the presence of a drop or particle surface that is impenetrable to the ions, an imposed electric field will cause ions with opposite charge to be attracted to the interface, as shown in Figure 2.1. These ions form a diffuse charge cloud or double layer near the interface, which is called a Debye layer. The imposed electric field exerts a body force on the double layer, and this drives a fluid motion. The fluid motion can have an important effect that depends on physical circumstances or application.

The canonical electrokinetic problem is when the surface has a fixed and constant charge. Two kinds of useful phenomena based on electrokinetics with wide applicability in analytical chemistry, microfluidics and other fields are electro-osmosis (a stationary surface surrounded by electrokinetic flow) and electrophoresis (particles freely suspended in an electrokinetic flow). Because of the fixed surface charge, classical electrokinetic phenomena are linear in the applied field, that is, the generated fluid motion grows linearly with the applied field strength for small applied fields.

The physical consequences of electrokinetic flow have been investigated in several canonical flow situations. For example, [9] investigated the electrokinetic attraction between spheres in an electrolyte. Other investigations include a study of electrokinetic flow at microelectrodes in [10], and the dynamics of an electrolyte film in [11]. Recently, the electrophoresis problem of colloidal systems was also analyzed in [12].

Another type of electrokinetic problem involves the charge at the interface being generated by the applied field itself. The name ‘induced-charge electro-osmosis’ (ICEO) was introduced by [13, 14] to describe nonlinear electrokinetic phenomena that occur when the surface charge is induced by the applied electric field. There is a large Ukrainian literature on induced-charge electro-osmosis (see, e.g., the review paper [15]), and interest in the area has recently revived due to important appli-
cations in microfluidics. In contrast to fixed charge electrokinetics, induced-charge phenomena are nonlinear in the applied field since the action of the electric field itself induces the diffuse charge layer.

The focus of our work is on the development of new models for the evolution of drops and vesicle membranes in electric fields together with accurate and efficient numerical methods for their solution. A motivation for this work comes from experiments on the directed motion and shape manipulation of vesicles by an applied electric field [16], and the recognition that the induced charge and flow are an example of induced-charge electro-osmosis.

Most of the existing work on electro-osmosis or electro-kinetics is for nondeformable surfaces with simple geometries (e.g., spherical). In this paper, we consider induced-charge electro-kinetic effects on the motion and shape of a drop or vesicle with a deformable interface. Specifically, we design an accurate and efficient numerical method for electro-kinetic flow with deformable interfaces. The existence of the thin Debye layer makes a numerical solution difficult, since the flow in the thin layer must be accurately resolved to accurately capture the time dependent deformation of the drop. We intend to use the slenderness of the layer to develop a fast and accurate ‘hybrid’ or multiscale numerical method that incorporates the asymptotic analysis of the boundary layer into a boundary integral numerical solution of the free boundary problem.

Leading order asymptotic solutions of the Debye layer ion concentration and flow has been obtained for simple geometries, e.g., a conducting sphere in an electrolyte [13]. More recently, the leading order ion concentration and flow for an arbitrary shaped rigid conducting surface was studied in [17]. As part of his analysis, Yariv introduces intrinsic, surface-fitted coordinates to obtain the Helmholtz-Smoluchowski slip velocity and fluid dynamics in the layer. An earlier analysis of the Debye layer problem in [18] also used intrinsic coordinates for moving and rigid particles. A more
general analytical approach to the problem of leaky dielectrics was recently presented in [19]. The analytical approach was also compared with [8]'s results and shown to be far superior to small perturbation theory in [3] or second order theory in [20].

The main difference between the present work and earlier studies is that we consider moving, deformable interfaces. Thus, we introduce intrinsic coordinates attached to a moving surface as in [21]. Our strategy is to solve inner and outer problems for the electric field separately with analytical and numerical methods, then match them. The fluid dynamics will be treated similarly. For this, it is necessary to adapt the classical boundary integral method for interfacial Stokes flow ([8, 22]) to take into account the jump in fluid, electric and osmotic stress across the double layer.

We intend to extend our method to study electro-kinetic motion of vesicles. A previous analytical study in [23] for vesicles considers a highly simplified model for the induced charge layer based on Schwan's formula [24]. This essentially treats the surface as a spherical capacitor which charges due to the action of the applied field. Our model provides a more description of the physics in the Debye layer.

The article is organized as follows: Chapter 2 provides a fundamental model of our problem and a systematic derivation of the problem in the limit of thin double layer. A leading order solution for time dependent electrohydrodynamics is presented. Chapter 3 discusses the fluid dynamics problem, including the Stokes equation and stress balance issues. Chapter 4 describes our adjusted boundary integral method. The asymptotic analysis for fluid field and small deformation theory is in Chapter 5 & 6. Chapter 7 & 8 include the numerical simulations for the case with fast charging time scale, while Chapter 9 discusses the model with considering the time dependent charging process. Finally, we list our summary and future work in Chapter 10.
CHAPTER 2
GOVERNING EQUATIONS IN THE ELECTRIC FIELD

2.1 Model
Consider an uncharged viscous drop suspended in a viscous surrounding fluid with an imposed uniform electric field. We assume that the fluids are polarizable, that is, either conducting or dielectric. In the absence of the drop, the electric field lines are parallel, but the presence of the conducting drop deforms the field in such a way that the lines are normal to the surface at the initial state (Figure 2.1, left, from [13]). This will cause the movement of free ions in the electrolyte. The electric field drives positive ions into a charge cloud on the bottom side of the drop, and negative ions to the top (see Figure 2.1). This induces an equal and opposite surface charge on the drop surface. The charge cloud increases in strength as long as there is a component of the electric field that is normal to the interface, so that ions are injected into the double layer. Steady state is reached when the normal component of the E-field at the interface tends to zero. Then, the charge cloud completely cancels or ‘screens’ the applied E-field (Figure 2.1, right, from [13]). The tangential field exerts a body force on the electrically charged fluid in the double layer, driving the ions and fluid to move. This results in a ‘slip’ velocity of fluid outside the double layer, with the velocity proportional to the local charge density. In the classical continuum model of the charge layer, the slip velocity is given by the Helmholtz-Smoluchowski formula:

\[ u_s = -\frac{\varepsilon_{el}}{\mu} \zeta E_t, \]

(2.1)

where \( \varepsilon_{el} \) is the permittivity of the electrolyte, \( \mu \) is the fluid viscosity, \( E_t \) is the tangential electric field just outside the double layer, and \( \zeta \) is the zeta-potential (a measure the electro-osmotic mobility with units of voltage). Classical electrokinetic
Figure 2.1  The initial state (left) and steady state (right) of a polarizable conducting particle or viscous drop immersed in an electrolyte, with a background uniform electric field applied. The field lines intersect normal to the drop surface at the initial state. After a charging time, a dipolar charge cloud forms and induces an equal and opposite surface charge on the conducting surface. The steady state (right) is achieved when no field lines penetrate the double layer on the drop surface.

Figure 2.2  The steady state of electro-osmotic fluid flow around a conducting particle with zero net charge.
phenomena are linear, which means \( u_s \propto E_t \), since the zeta potential is assumed to be a material constant. Nonlinear electro-osmotic flow (also known as induced-charge electro-osmosis, or ICEO) results from an E-field acting on its own induced charge. In this case, \( \zeta \propto E_t \) and \( u_s \propto E_t^2 \). A uniform electric field drives the fluid from the ‘poles’ of a particle to the ‘equator’ at the steady state, as shown in Figure 2.2.

A diffuse charge cloud forms at the surface as ions of opposite charge are attracted toward the surface. Thus, Debye layers exist both inside and outside the drop at the interface. Outside the layers, the ion charge density is zero, which means the number density of positive ions \( n^{(+)} \) equals the number density of negative ions \( n^{(-)} \). We present the main equations for the electric field and ion density following [13]. Define the electric potential \( \phi \) by \( \mathbf{E} = -\nabla \phi \). Since there is no net charge, the electric potential \( \phi \) outside of the Debye layer satisfies Laplace equation:

\[
\nabla^2 \phi = 0, \quad \text{for } \mathbf{x} \notin \Omega_0, \tag{2.2}
\]

where \( \Omega_0 \) is the Debye layer. The boundary condition as \( |\mathbf{x}| \to \infty \) is that for a uniform field, i.e.,

\[
\phi = -E_\infty x, \tag{2.3}
\]

where \( E_\infty \) is the imposed field, \( \mathbf{E} = (E_\infty, 0, 0) \) and \( \mathbf{x} = (x, y, z) \). Within the Debye layer there is a net charge density \( (n^{(+)} - n^{(-)})e \), where \( e \) is the ion charge. Therefore, within the Debye layer, the electric potential satisfies Poisson’s equation

\[
\nabla^2 \phi = -\frac{(n^{(+)} - n^{(-)})e}{\varepsilon_{el}}, \quad \mathbf{x} \in \Omega_0. \tag{2.4}
\]

The ion number densities also satisfy conservation equations:

\[
\frac{\partial n^{(\pm)}}{\partial t} + \nabla \cdot (n^{(\pm)} \mathbf{v}_\pm) = 0, \tag{2.5}
\]
where the velocities of the two kinds of ions are

\[ \mathbf{v}_\pm = \mp be \nabla \phi - k_B T b \nabla \ln n^{(\pm)} + \mathbf{u}. \]  

(2.6)

Here \( \mathbf{u} \) is the local fluid velocity, \( b \) is the ion mobility, \( k_B \) is the Boltzmann constant and \( T \) is the temperature. Ion velocities are composed of three parts: electrostatic forcing, diffusion down density gradients and the local fluid velocity.

We are interested in the moving boundary problem, and assume the interface is impermeable to ions, thus, ions obey no-flux condition on the boundary \( \Gamma \)

\[ \mathbf{n} \cdot (\mathbf{v}_\pm - \mathbf{u})|_\Gamma = 0, \]  

(2.7)

where \( \mathbf{n} \) is the outward normal. The condition is also equivalent to the boundary condition that the normal component of the current density must vanish at the interface. And it expresses the assumption that no surface charge distribution can build up. To understand that more clearly, we use expression (2.6) to write (2.7) as

\[ \mathbf{n} \cdot \left( \mp be \nabla \phi - k_B T b \nabla \ln n^{(\pm)} \right)|_\Gamma = 0, \]  

(2.8)

which means the normal diffusive and electromigrative currents must cancel each other at the interface.

The interface motion is given by the kinematic condition

\[ \frac{d\mathbf{x}}{dt} = \mathbf{u} \cdot \mathbf{n}, \]  

(2.9)

where \( \mathbf{x}(\xi, t) \) is a parametric representation of the interface.

Next, we simplify these equations in order to analyze the time dependent charge densities. Adding and subtracting the two equations in (2.5) gives the dimensional electrokinetic equations:

\[ \frac{\partial \rho}{\partial t} + D \nabla^2 \rho - D \nabla^2 \rho - e b \nabla \cdot [\rho \nabla \phi] + \mathbf{u} \cdot \nabla \rho = 0, \]  

(2.10)
\[
\frac{\partial c^e}{\partial t} - D \nabla^2 c^e - e b \nabla \cdot [c^e \nabla \phi] + \mathbf{u} \cdot \nabla c^e = 0, \quad (2.11)
\]

where \( D = k_B T b \) is the ion diffusivity, and \( c^\rho = n^{(+)} - n^{(-)} \) is the ion charge density, \( c^e = n^{(+)} + n^{(-)} - 2n^{(0)} \) is the difference between total ion concentration and far field ion concentration \( 2n^{(0)} \). The quantity \( \lambda_D = 1/\kappa \) has dimension of length and corresponds to the thickness of the Debye layer. The Debye length is written in terms of fundamental quantities as ([13])

\[
\lambda_D = \left( \frac{\varepsilon_e k_B T}{2n^{(0)} e^2} \right)^{1/2},
\]

thus, \( \kappa^2 = \frac{2e^2n^{(0)}}{\varepsilon_e k_B T} \).

Equation (2.4) is written in terms of \( c^\rho \) as

\[
\nabla^2 \phi = - \frac{c^\rho e}{\varepsilon_e}
\]

The no-flux boundary conditions become

\[
\mathbf{n} \cdot \nabla c^\rho |_\Gamma = - \frac{e}{k_B T} (2n^{(0)} + c^e) \mathbf{n} \cdot \nabla \phi |_\Gamma,
\]

\[
\mathbf{n} \cdot \nabla c^e |_\Gamma = - \frac{e}{k_B T} c^\rho \mathbf{n} \cdot \nabla \phi |_\Gamma.
\]

The other two boundary conditions used for determining the unknowns are listed below.

The potentials in different sides of the surface must be continuous at the interfaces:

\[
\phi_+ |_\Gamma = \phi_- |_\Gamma,
\]

where \( \phi_\pm \) mean potentials in ‘+’ and ‘−’ regions.

The normal component of the displacement must be continuous at the interface,

\[
\varepsilon_+ \mathbf{n} \cdot \nabla \phi_+ |_\Gamma = \varepsilon_- \mathbf{n} \cdot \nabla \phi_- |_\Gamma,
\]

(2.17)
where \( \varepsilon_{\pm} \) mean permittivities in ‘+’ and ‘−’ regions. This condition is based on the fact that no surface charge can appear.

Equations (2.2, 2.3, 2.10, 2.11, 2.13 - 2.17) determine the electric field and ion concentration in a given problem. This will be coupled to the equations for the fluid flow \( \mathbf{u} \). The electric field generated by the ions in the Debye layer will introduce forcing terms in the fluid equations, and terms in the interface boundary conditions. These are discussed in Chapter 3.

2.2 Non-dimensionalization

We choose the length scale \( L \) to be the initial undeformed drop radius. There are three important time scales. These are motivated by the solution to canonical problems in simple geometries ([13]). The Debye time \( T_D \) is defined as the time for diffusion across the double layer of thickness \( \lambda_D \). It is given by \( T_D = \lambda_D^2 / D = (D\kappa^2)^{-1} \). Another important time scale is the charging time \( T_C \). When the electric field is first applied, mobile ions from the fluid are driven into the Debye layer. The charge cloud grows as long as fluid lines penetrate the layer and more ions are injected into it. The charging time \( T_C \) is defined as the time for a steady state to be achieved. This occurs when the field lines no longer penetrate the layer and ion flux into the layer decreases to zero. The charging time \( T_C \) satisfies \( T_C = T_D L / \lambda_D = \lambda_D L / D \). Note that \( T_D \ll T_C \). The third time scale is that for fluid motion, which is given by \( T_F = L / U \), where \( U \) is a representative velocity in the problem. We take \( U \) to be the Helmholtz-Smoluchowski slip velocity \( U = \varepsilon_{el} E_{\infty}^2 L / \mu \), where \( E_{\infty} \) is the imposed electric field and \( \mu \) is the viscosity of the exterior fluid. This slip velocity comes from an analysis of the induced fluid velocity when an electric field is applied to an initially uncharged conducting sphere immersed in an electrolyte. A thin dipole charge layer of thickness \( \lambda_D \ll L \) forms at the surface of the conductor. The imposed field exerts a force on the ions in the layer (or, equivalently, a body force on the electrically charged fluid), and this drives
a fluid motion. This electro-osmotic flow appears as a slip velocity of magnitude $U$ just outside the screening layer of width $\lambda_D$. A table from [13] with representative values of the time scales is given in Table 2.1.

**Table 2.1** Representative Values for Electro-Osmotic Flow

<table>
<thead>
<tr>
<th>Material properties of aqueous solution</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity</td>
<td>$\mu$</td>
<td>$10^{-2}$</td>
<td>g cm$^{-1}$s$^{-1}$</td>
</tr>
<tr>
<td>Dielectric constant</td>
<td>$\varepsilon_{el} \approx 80\varepsilon_0$</td>
<td>$7 \times 10^{-5}$</td>
<td>g cm V$^{-2}$s$^{-2}$</td>
</tr>
<tr>
<td>Ion diffusivity</td>
<td>$D$</td>
<td>$10^{-5}$</td>
<td>cm$^2$s$^{-1}$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Experimental parameters</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Drop radius</td>
<td>$L$</td>
<td>10</td>
<td>$\mu$m</td>
</tr>
<tr>
<td>Applied field</td>
<td>$E_\infty$</td>
<td>100</td>
<td>V cm$^{-1}$</td>
</tr>
<tr>
<td>Debye length</td>
<td>$\lambda_D = (\frac{\varepsilon_{el}k_BT}{2n^{(0)}e^2})^{1/2}$</td>
<td>10</td>
<td>nm</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Characteristic scales</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Slip velocity</td>
<td>$U = \frac{\varepsilon_{el}E_\infty^2L}{\mu}$</td>
<td>0.7</td>
</tr>
<tr>
<td>Debye time</td>
<td>$T_D = \frac{\lambda_D^2}{D}$</td>
<td>$10^{-7}$</td>
</tr>
<tr>
<td>Charging time</td>
<td>$T_C = \frac{\lambda_D L}{D}$</td>
<td>$10^{-4}$</td>
</tr>
<tr>
<td>Fluid motion time</td>
<td>$T_F = \frac{L}{U}$</td>
<td>$10^{-2}$</td>
</tr>
</tbody>
</table>

Our strategy is to use Debye time scale to nondimensionalize the governing equations and when appropriate we will rescale by charging time later. So we use scales as follows:

$$t = (D\kappa^2)^{-1}\tilde{t}, \quad r = L_0\tilde{r}, \quad \phi = \Phi_0\tilde{\phi}, \quad \mathbf{u} = U\tilde{\mathbf{u}}, \quad \phi^o = 2n^{(0)}\Psi\tilde{\phi}^o, \quad c^e = 2n^{(0)}\Psi^2\tilde{c}^e$$ (2.18)

and introduce the Péclet number $Pe = \frac{UL_0}{D}$, the small parameter $\epsilon = \frac{\lambda_D}{L_0}$, and the dimensionless surface potential $\Psi = \frac{e\Phi_0}{k_BT}$. Note that we scale $c^o$ by $\Psi$ while we scale
$c^e$ by $\Psi^2$ because we need them satisfy the dominant balance in (2.11). Also, when we first consider the limit of small dimensionless surface potential $\Psi \ll 1$, the system will be significantly simplified as $\tilde{c}^\rho$ is coupled to $\tilde{c}^e$ by terms of $O(\Psi^2)$ in equation (2.22) and boundary condition (2.24), and $c^e = n^{(+)} + n^{(-)} - 2n^{(0)}$ is smaller than $c^\rho = n^{(+)} - n^{(-)}$ by a factor $\Psi$.

The dimensionless outer equation for potential is (dropping tilde)

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

with far-field boundary condition

$$\phi = -\tilde{E}_\infty x, \hspace{1em} as \hspace{1em} |x| \to \infty,$$

where $\tilde{E}_\infty = \frac{L_0}{\Phi_0} E_\infty$, we next consider the inner equations.

The dimensionless Poisson’s equation and conservation equations are (dropping the tilde):

$$\epsilon^2 \nabla^2 \phi = -c^\rho,$$  \hspace{1em} (2.21)

$$\frac{\partial c^\rho}{\partial t} + Pe\epsilon^2 \mathbf{u} \cdot \nabla c^\rho + c^\rho - \epsilon^2 \nabla^2 c^\rho - \epsilon^2 \Psi^2 \nabla \cdot [c^e \nabla \phi] = 0,$$  \hspace{1em} (2.22)

$$\frac{\partial c^e}{\partial t} + Pe\epsilon^2 \mathbf{u} \cdot \nabla c^e - \epsilon^2 \nabla^2 c^e - \epsilon^2 \nabla \cdot [c^\rho \nabla \phi] = 0.$$  \hspace{1em} (2.23)

The no-flux boundary conditions become

$$\mathbf{n} \cdot \nabla c^\rho|_\Gamma = -(1 + \Psi^2 c^e) \mathbf{n} \cdot \nabla \phi|_\Gamma,$$  \hspace{1em} (2.24)

$$\mathbf{n} \cdot \nabla c^e|_\Gamma = -c^\rho \mathbf{n} \cdot \nabla \phi|_\Gamma.$$  \hspace{1em} (2.25)

Also, for the potentials in different sides of the surface, the boundary conditions are the continuity of electric potential and the continuity of the displacement component normal to the surface

$$\phi^+|_\Gamma = \phi^-|_\Gamma,$$  \hspace{1em} (2.26)
\[ \varepsilon_+ \mathbf{n} \cdot \nabla \phi_+ |_{\Gamma} = \varepsilon_- \mathbf{n} \cdot \nabla \phi_- |_{\Gamma}, \quad (2.27) \]

We consider \( Pe = O(1) \) (which is a representative magnitude for the physical problems of interest) and assume a weak applied field so that \( \Psi \ll 1 \). Under these assumptions equations for \( c^\rho \) are decoupled from that for \( c^e \) (this is verified in the next section). We therefore ignore equation (2.11) and terms containing \( c^e \), and solve for \( c^\rho \) and \( \phi \).

### 2.3 A Spherical Drop in an Electrolyte

We first consider a model problem for a non-deforming spherical drop of unit radius immersed in an electrolyte solution. The drop is also an electrolyte, which means a Debye layer forms on the interior. A solution for equations (2.19 - 2.27) for the electric field and ion concentration is obtained by the method of matched asymptotic expansions. The equations are first new written in a spherical coordinate system \((r, \theta, \varphi)\). Since the problem is axisymmetric there is no dependence of the solution on \( \varphi \), and \( \theta \) is being measured from the direction of the electric field (clockwise in Fig. 2.3). An inner variable \( N = \frac{(r-1)}{\varepsilon} \) is introduced, and we solve the leading order inner and outer equations in the limit \( \varepsilon \to 0 \). Appropriate boundary conditions for these equations are provided by matching the solutions.

For the model problem, the solutions can be obtained analytically. Our interest is in extending the analysis to a deformed drop in an imposed electric field, and for this more complicated problem, it is not possible to find the outer solution analytically. However, a closed form expression for the inner solution is obtained (this expression has undetermined functions that are fixed by matching to the outer solution). We propose to use a boundary integral numerical method to compute the outer solution. Boundary conditions for the boundary integral calculation are provided by matching to the inner solution.
Figure 2.3 The 3-D axisymmetric model for a viscous drop suspended in an electrolyte with a DC field applied. \( \phi_{\pm} \) are the potentials within the double layer in ‘\( \pm \)’ regions, and \( \phi_{o\pm} \) are the outer potentials outside the layers.

We also need to consider the fluid dynamics. A solution to the fluid equations is obtained by a similar matched asymptotic approach. This is discussed in Chapter 3.

Let \( \phi_{o+} \) denote the outer solution in the fluid region exterior to the drop, and \( \phi_{o-} \) the outer solution in the interior region. Also, we denote the inner solution on the exterior of the drop interface by \( \phi_+ \), and that on the interior by \( \phi_- \) (see Figure 2.3). We assume the outer solution has an expansion of the form:

\[
\phi_{o\pm} = \phi_{o\pm}^{(0)} + \epsilon \phi_{o\pm}^{(1)} + \epsilon^2 \phi_{o\pm}^{(2)} + \ldots
\]  

(2.28)

As mentioned, outside the Debye layer the number density of positive and negative ions are equal, so that \( c_\rho = 0 \) in the outer region and the leading order equation for \( \phi_{o\pm} \) is (see (2.21))

\[
\nabla^2 \phi_{o\pm}^{(0)} = 0
\]  

(2.29)
The far-field boundary condition is

\[ \phi_o = -\tilde{E}_\infty x, \quad as \ |x| \to \infty, \]  

(2.30)

where \( \tilde{E}_\infty = \frac{L_0}{\Phi_0} E_\infty \) is now the dimensionless far-field value (henceforth we drop the tilde). In the case of a spherical drop it is possible to derive a general solution to (2.29) and (2.30) as

\[ \phi_{o\pm} = -(A_{\pm}(t)r + \frac{B_{\pm}(t)}{r^2}) \cos \theta, \]  

(2.31)

where \( A_+ = -E_\infty \) and, since we require \( \phi_o \) to be bounded at \( r = 0 \), \( B_- = 0 \). We note that in the steady state (i.e., when there is no charging of the interface) the electric field lines are tangential to the drop surface, so that

\[ \left. \frac{\partial \phi_{o\pm}}{\partial r} \right|_{r=1} = 0. \]  

(2.32)

Therefore, \( A_- = 0 \) and \( B_+ = -E_\infty / 2 \), the analytic solution to the outer problem is

\[ \phi_{o+} = E_\infty (r + \frac{1}{2r^2}) \cos \theta, \]  

(2.33)

\[ \phi_{o-} = 0. \]  

(2.34)

However, in general we are interested in the time dependent case when the interface is still charging and the solution to the outer problem is

\[ \phi_{o+} = (E_\infty r - \frac{B_+(t)}{r^2}) \cos \theta, \]  

(2.35)

\[ \phi_{o-} = -A_-(t) r \cos \theta, \]  

(2.36)

and \( B_+(t), A_-(t) \) need to be determined by matching to the inner problem. This is considered in the next section.
2.4 Inner Problem

Before expanding the inner electric and fluid fields, we simplify the problem as that the Debye length inside the drop is in the same order of the Debye length outside the drop. This assumption lets us expand all fields with the same small parameter $\epsilon = \epsilon_+$. With considering the definition of Debye length in (2.12), we have

$$\frac{\lambda_{D-}}{\lambda_{D+}} = \sqrt{\frac{\varepsilon_- n_+^{(0)}}{\varepsilon_+ n_-^{(0)}}},$$

(2.37)

where $n_+^{(0)}$ and $n_-^{(0)}$ are the far field or uniform equilibrium ion concentration in the exterior/interior ($' +' /'-'$) of the drop. With the definition of partial electrical conductivity of each species, it’s convenient to present the expression for total electrical conductivity as (for a symmetric $z:z$ electrolyte)

$$\sigma = 2e^2 n^{(0)} b.$$

(2.38)

The ratio of parameters can be simplified using both the Einstein electrical mobility relation and Einstein-Stokes relation

$$D = k_B T b = \frac{k_B T}{6 \pi \mu d},$$

(2.39)

where $\mu$ is the fluid viscosity and $d$ is the ionic radii. Assuming the equal ionic radii in both liquids, Equations (2.37, 2.38, 2.39) yield

$$\frac{\lambda_{D-}}{\lambda_{D+}} = \sqrt{\frac{\alpha}{\lambda K}}, \quad \frac{n_-^{(0)}}{n_+^{(0)}} = \lambda K,$$

(2.40)

with ratios of the internal and external values of permittivities, conductivities and viscosities as following:

$$\alpha = \frac{\varepsilon_-}{\varepsilon_+}, \quad K = \frac{\sigma_-}{\sigma_+}, \quad \lambda = \frac{\mu_-}{\mu_+}.$$

(2.41)
To make consistent scales for both outside and inside of the drop, we use the outside far field ion concentration \( n_+^{(0)} \) for rescaling the charge densities in both \('+\)' and \'-\)' regions: \( \rho_\pm' = 2n_+^{(0)} \Psi_\pm, \rho_\pm'' = 2n_+^{(0)} \Psi^2 \xi_\pm'. \)

Since we are interested in drop dynamics on the time scale of the charging time \( T_C = T_D/\epsilon \), we introduce a rescaled time \( \tau = \epsilon t \), with the assumption \( \Psi \ll 1, \epsilon \ll 1 \) and \( Pe = O(1) \). Equations (2.21, 2.22, 2.24) for \( \rho^o \) become at leading order

\[
\begin{align*}
\epsilon^2 \nabla^2 \phi_+ &= -\rho_+^o, \\
\epsilon^2 \nabla^2 \phi_- &= -\frac{1}{\alpha} \rho_-^o, \\
\epsilon \frac{\partial \rho_+^o}{\partial t} + \rho_+^o - \epsilon^2 \nabla^2 \rho_+^o &= 0, \\
\epsilon \frac{\alpha}{K} \frac{\partial \rho_-^o}{\partial t} + \rho_-^o - \epsilon^2 \frac{\alpha}{\lambda K} \nabla^2 \rho_-^o &= 0,
\end{align*}
\]

and no-flux boundary conditions

\[
\begin{align*}
n \cdot \nabla \rho_+^o |_\Gamma &= -n \cdot \nabla \phi_+ |_\Gamma, \\
n \cdot \nabla \rho_-^o |_\Gamma &= -\lambda K n \cdot \nabla \phi_- |_\Gamma,
\end{align*}
\]

where we keep the Laplacian term because we expect \( \rho^o \) and the potential \( \phi \) to have large derivatives in the normal direction in the Debye layer. To account for this, we introduce a rescaled normal coordinate \( N \) as

\[
r = 1 \pm \epsilon N,
\]

where the \'+\' is taken in the region exterior to the drop boundary, and the \'-\' in the interior.

In terms of the rescaled coordinate, the interfacial boundary conditions of continuity of electric potential and continuity of normal component of displacement become

\[
\phi_+ = \phi_-,
\]
\[
\frac{\partial \phi_+}{\partial N} = -\alpha \frac{\partial \phi_-}{\partial N}.
\] (2.50)

In our asymptotic analysis, we first expand the inner charge density and potential as

\[
\phi_\pm = \phi^0_\pm + \epsilon \phi^1_\pm + \ldots, \quad (2.51)
\]

\[
c^\phi_\pm = c^0_\pm + \epsilon c^1_\pm + \ldots. \quad (2.52)
\]

After rescaling the electrokinetic equations (2.44, 2.45), Poisson’s equations (2.42, 2.43) and boundary conditions (2.46, 2.47) in normal direction, we can obtain the inner equations for \(O(1)\) and \(O(\epsilon)\) terms:

**O(1):**

\[
\frac{\partial^2 c^0_+}{\partial N^2} - c^0_+ = 0, \quad (2.53)
\]

\[
\frac{\alpha}{\lambda K} \frac{\partial^2 c^0_-}{\partial N^2} - c^0_- = 0, \quad (2.54)
\]

\[
\frac{\partial^2 \phi^0_+}{\partial N^2} + c^0_+ = 0, \quad (2.55)
\]

\[
\frac{\partial^2 \phi^0_-}{\partial N^2} + \frac{1}{\alpha} c^0_- = 0, \quad (2.56)
\]

with no-flux boundary conditions on \(N = 0\):

\[
\frac{\partial c^0_+}{\partial N} = -\frac{\partial \phi^0_+}{\partial N}, \quad (2.57)
\]

\[
\frac{\partial c^0_-}{\partial N} = -\lambda K \frac{\partial \phi^0_-}{\partial N}. \quad (2.58)
\]

**O(\epsilon):**

\[
\frac{\partial c^0_+}{\partial t} - 2 \frac{\partial c^0_+}{\partial N} - \frac{\partial^2 c^1_+}{\partial N^2} + c^1_+ = 0, \quad (2.59)
\]

\[
\frac{\alpha}{K} \frac{\partial c^0_-}{\partial t} + 2 \frac{\alpha}{\lambda K} \frac{\partial c^0_-}{\partial N} - \frac{\alpha}{\lambda K} \frac{\partial^2 c^1_-}{\partial N^2} + c^1_- = 0, \quad (2.60)
\]

\[
2 \frac{\partial \phi^0_+}{\partial N} + \frac{\partial^2 \phi^1_+}{\partial N^2} = -c^1_+, \quad (2.61)
\]
\[-2 \frac{\partial \phi_0}{\partial N} + \frac{\partial^2 \phi_1}{\partial N^2} = -\frac{n_+^{(0)}}{n_-^{(0)}} c_-, \quad (2.62)\]

with no-flux boundary conditions on \( N = 0 \):

\[
\begin{align*}
\frac{\partial c_1^+}{\partial N} &= -\frac{\partial \phi_1^+}{\partial N}, \quad (2.63) \\
\frac{\partial c_1^-}{\partial N} &= -\lambda K \frac{\partial \phi_1^-}{\partial N}. \quad (2.64)
\end{align*}
\]

The outer solutions are given by (2.31).

\textbf{O}(1) inner solution:

From (2.53, 2.54, 2.55, 2.56), we get

\[
\begin{align*}
c_0^+ &= C_0^+ (\theta, t) e^{-N}, \quad (2.65) \\
c_0^- &= C_0^- (\theta, t) e^{-\sqrt{\frac{\alpha}{\lambda K}} N}, \quad (2.66) \\
\phi_0^+ &= -C_0^+ (\theta, t) e^{-N} + D_0^+ (\theta, t) N + E_0^+ (\theta, t), \quad (2.67) \\
\phi_0^- &= -\frac{1}{\lambda K} C_0^0 (\theta, t) e^{-\sqrt{\frac{\alpha}{\lambda K}} N} + D_0^0 (\theta, t) N + E_0^0 (\theta, t), \quad (2.68)
\end{align*}
\]

where \( C_0^0 (\theta, t) \) is the boundary value at \( N = 0 \). And (2.57, 2.58) give

\[
D_0^0 = 0, \quad (2.69)
\]

which agrees with [13]'s result \( D = O(\epsilon) \).

Boundary conditions at the interface \( N = 0 \) are

(1) Continuity of the displacement component normal to the surface:

\[
\frac{\partial \phi_0^+}{\partial N} = -\alpha \frac{\partial \phi_0^-}{\partial N}. \quad (2.70)
\]

Thus, we get

\[
C_0^+ = -\sqrt{\frac{\alpha}{\lambda K}} C_0^-. \quad (2.71)
\]
(2) Continuity of potential:

\[-C_+^0 + E_+^0 = -\frac{1}{\lambda K} C_0^0 + E_0^0.\] (2.72)

Matching of inner and outer solutions gives

\[\phi^0_{o+}(1) = (E_\infty - B^0_+) \cos \theta = E_+^0,\] (2.73)

\[\phi^0_{o-}(1) = -A_0^0 \cos \theta = E_0^- .\] (2.74)

**O(\epsilon) inner solution:**

Equations (2.59, 2.60, 2.61, 2.62) give the solutions:

\[c_+^1 = \left(-C_+^0 - \frac{1}{2} \frac{\partial C_0^0}{\partial t}\right) Ne^{-N} + C_+^1 e^{-N},\] (2.75)

\[c_-^1 = \left(\frac{\alpha}{\lambda K} C_0^- - \frac{1}{2} \frac{\alpha}{K} \sqrt{\frac{\alpha}{\lambda K}} \frac{\partial C_0^0}{\partial t}\right) Ne^{-\sqrt{\frac{\lambda K}{\alpha}} N} + C_-^1 e^{-\sqrt{\frac{\lambda K}{\alpha}} N},\] (2.76)

\[\phi_+^1 = \left(C_+^0 + \frac{1}{2} \frac{\partial C_0^0}{\partial t}\right) Ne^{-N} + \left(\frac{\partial C_+^0}{\partial t} - C_+^1\right) e^{-N} + D_+^1 N + E_+^1 ,\] (2.77)

\[\phi_-^1 = \left(-\frac{\alpha}{\lambda^2 K^2} C_0^- + \frac{1}{2} \frac{1}{K} \left(\frac{\alpha}{\lambda K}\right)^{3/2} \frac{\partial C_0^-}{\partial t}\right) Ne^{-\sqrt{\frac{\lambda K}{\alpha}} N}
+ \left(\frac{2}{\lambda K} \sqrt{\frac{\alpha}{\lambda K}} \left(1 - \frac{\alpha}{\lambda K}\right) C_-^0 + \frac{\alpha^2}{\lambda K^3} \frac{\partial C_0^-}{\partial t} - \frac{1}{\lambda K} C_-^1\right) e^{-\sqrt{\frac{\lambda K}{\alpha}} N}
+ D_-^1 N + E_-^1 ,\] (2.78)

where \(C_\pm^1\) is the boundary value of \(c_\pm^1\) on \(N = 0\).

Equations (2.63, 2.64) give

\[D_+^1 = \frac{\partial C_+^0}{\partial t},\] (2.79)

\[D_-^1 = \frac{1}{K} \left(\frac{\alpha}{\lambda K}\right)^{3/2} \frac{\partial C_0^-}{\partial t} + \frac{2}{\lambda K} \left(1 - \frac{\alpha}{\lambda K}\right) C_0^- ,\] (2.80)

The boundary conditions on \(N = 0\) are

(1) Continuity of the displacement component normal to the surface:

\[\frac{\partial \phi_+^1}{\partial N} = -\alpha \frac{\partial \phi_-^1}{\partial N}.\] (2.81)
Continuity of potential:

\[
\frac{\partial C_0}{\partial t} - C_+^1 + E_+^1 = \frac{2}{\lambda K} \sqrt{\frac{\alpha}{\lambda K}} \left(1 - \frac{\alpha}{\lambda K}\right) C_0^0 + \frac{\alpha^2}{\lambda^2 K^3} \frac{\partial C_0^-}{\partial t} - \frac{1}{\lambda K} C_-^1 + E_-. \tag{2.82}
\]

Matching of inner and outer solutions is

\[
\phi_{o\pm}(r \to 1) = \phi_{\pm}(N \to \infty), \tag{2.83}
\]

with

\[
\phi_{o\pm}(r \to 1) = \phi_{o\pm}(1) + \frac{\partial \phi_{o\pm}}{\partial r} \bigg|_{r=1}(r-1) + \ldots
\]

\[
= - [(A_0^1 + B_0^1) \cos \theta + \epsilon(A_1^1 + B_1^1) \cos \theta + \ldots] - [(A_0^1 - 2B_0^1) + \epsilon(A_1^1 - 2B_1^1)] \cos \theta(\pm \epsilon N) + \ldots, \tag{2.84}
\]

and

\[
\phi_{\pm}(N \to \infty) = \phi_{0\pm}(N \to \infty) + \epsilon \phi_{1\pm}(N \to \infty) + \ldots. \tag{2.85}
\]

Thus, for \(O(\epsilon)\) we have

\[
-(A_1^1 + B_1^1) \cos \theta - (A_0^1 - 2B_0^1) \cos \theta \cdot N = D_+^1 N + E_+^1, \tag{2.86}
\]

\[
-(A_1^1 + B_1^1) \cos \theta + (A_0^1 - 2B_0^1) \cos \theta \cdot N = D_-^1 N + E_-^1, \tag{2.87}
\]

which give

\[
\frac{\partial C_0^0}{\partial t} = -(A_0^0 - 2B_0^1) \cos \theta, \tag{2.88}
\]

\[
\frac{1}{K} \left(\frac{\alpha}{\lambda K}\right)^{3/2} \frac{\partial C_0^-}{\partial t} = \frac{2}{\lambda K} \left(1 - \frac{\alpha}{\lambda K}\right) C_0^- = (A_0^0 - 2B_0^1) \cos \theta. \tag{2.89}
\]

Solving equations (2.71 - 2.74) and (2.88, 2.89), we get the ODE for \(C_0^0\):

\[
\left(\frac{1}{2} \sqrt{\frac{\alpha}{\lambda K}} + \frac{1}{K} \left(\frac{\alpha}{\lambda K}\right)^{3/2}\right) \frac{\partial C_0^0}{\partial t} + \left(\sqrt{\frac{\alpha}{\lambda K}} + \frac{1}{\lambda K} \left(3 - \frac{2\alpha}{\lambda K}\right)\right) C_0^- = -\frac{3}{2} E_\infty \cos \theta. \tag{2.90}
\]
Assuming that the initial condition is \( C_0^0(\theta, 0) = 0 \), then we can find explicit solutions for \( C_\pm^0, D_\pm^1, A_\pm^0, B_\pm^0 \) and \( E_\pm^0 \):

\[
C_-^0 = \frac{3}{2S_2} (e^{-\frac{S_2}{S_1}t} - 1) E_\infty \cos \theta, \quad (2.91)
\]

\[
C_+^0 = -\frac{3}{2S_2} \sqrt{\frac{\alpha}{\lambda K}} (e^{-\frac{S_2}{S_1}t} - 1) E_\infty \cos \theta, \quad (2.92)
\]

\[
A_-^0 = \left[ \left( -\frac{3}{2S_1 K} \left( \frac{\alpha}{\lambda K} \right)^{3/2} + \frac{3}{S_2 \lambda K} \left( 1 - \frac{\alpha}{\lambda K} \right) \right) e^{-\frac{S_2}{S_1}t} \right.
\]
\[ -\frac{3}{S_2 \lambda K} \left( 1 - \frac{\alpha}{\lambda K} \right) \] \( E_\infty \),

\( (2.93) \)

\[
B_+^0 = \frac{3}{4S_1} \sqrt{\frac{\alpha}{\lambda K}} e^{-\frac{S_2}{S_1}t} E_\infty - \frac{E_\infty}{2}, \quad (2.94)
\]

\[
E_+^0 = \left( -\frac{3}{4S_1} \sqrt{\frac{\alpha}{\lambda K}} e^{-\frac{S_2}{S_1}t} + \frac{3}{2} \right) E_\infty \cos \theta, \quad (2.95)
\]

\[
E_-^0 = -\left[ \left( -\frac{3}{2S_1 K} \left( \frac{\alpha}{\lambda K} \right)^{3/2} + \frac{3}{S_2 \lambda K} \left( 1 - \frac{\alpha}{\lambda K} \right) \right) e^{-\frac{S_2}{S_1}t} \right.
\]
\[ -\frac{3}{S_2 \lambda K} \left( 1 - \frac{\alpha}{\lambda K} \right) \] \( E_\infty \cos \theta, \quad (2.96)

\[
D_+^1 = \frac{3}{2S_1} \sqrt{\frac{\alpha}{\lambda K}} e^{-\frac{S_2}{S_1}t} E_\infty \cos \theta, \quad (2.97)
\]

\[
D_-^1 = \left[ \left( -\frac{3}{2S_1 K} \left( \frac{\alpha}{\lambda K} \right)^{3/2} + \frac{3}{S_2 \lambda K} \left( 1 - \frac{\alpha}{\lambda K} \right) \right) e^{-\frac{S_2}{S_1}t} \right.
\]
\[ -\frac{3}{S_2 \lambda K} \left( 1 - \frac{\alpha}{\lambda K} \right) \] \( E_\infty \cos \theta, \quad (2.98)

where

\[
S_1 = \frac{1}{2} \sqrt{\frac{\alpha}{\lambda K}} + \frac{1}{K} \left( \frac{\alpha}{\lambda K} \right)^{3/2}, \quad (2.99)
\]

\[
S_2 = \sqrt{\frac{\alpha}{\lambda K}} + \frac{1}{\lambda K} \left( 3 - \frac{2\alpha}{\lambda K} \right). \quad (2.100)
\]

The steady state limit is \( t \to \infty \), which corresponds to the Debye layer being fully charged. The equations simplify to

\[
\phi_+^0 = -\frac{3}{2S_2} \sqrt{\frac{\alpha}{\lambda K}} E_\infty \cos \theta e^{-N} + \frac{3}{2} E_\infty \cos \theta, \quad (2.101)
\]

\[
\phi_-^0 = \frac{3}{2S_2 \lambda K} E_\infty \cos \theta e^{-\sqrt{\frac{\alpha}{\alpha}} N} + \frac{3}{S_2 \lambda K} \left( 1 - \frac{\alpha}{\lambda K} \right) E_\infty \cos \theta. \quad (2.102)
\]
In this limit, the E-field lines will have no normal component to the drop surface, as shown in Figure 2.1 (right). We could also write all the coefficients into the general normal and tangential coordinates for arbitrary shape of the drop. Here, we only use the leading order solutions of the coefficients for the small deformation theory, when the spherical drop shape is assumed, thus, we write them with \( \cos \theta \) for simplicity.

### 2.5 \( O(1) \) Applied Field

Next we relax the assumption that the applied electric field is weak and consider \( \Psi = O(1) \). Also, it is convenient to use the original ion density equations (2.5) rather than the equations for \( c^o \) and \( c^e \). The dimensional ion density equations for \( ^+ \) and \( ^- \) regions are

\[
\frac{\partial n_+^{(\pm)}}{\partial t} + \mathbf{u}_+ \cdot \nabla n_+^{(\pm)} + \nabla \cdot (\mp b_+ c n_+^{(\pm)} \nabla \phi_+ - k_B T b_+ \nabla n_+^{(\pm)}) = 0, \tag{2.103}
\]

\[
\frac{\partial n_-^{(\pm)}}{\partial t} + \mathbf{u}_- \cdot \nabla n_-^{(\pm)} + \nabla \cdot (\pm b_- c n_-^{(\pm)} \nabla \phi_- - k_B T b_- \nabla n_-^{(\pm)}) = 0. \tag{2.104}
\]

The leading order solution for the quasi-steady state problem is solved in this section after introducing intrinsic coordinates and rescaling variables.

#### 2.5.1 Intrinsic Coordinates

The first step in generalizing the analysis to a deformable drop is to write the governing equations in surface-fitted or intrinsic coordinates. We introduce intrinsic coordinates \((\xi_1, \xi_2, n)\), where \( \xi_1 \) and \( \xi_2 \) are directions aligned with the principal directions of curvature of the moving interface \( \Gamma \), and \( n \) is distance along normal measured from \( \Gamma \). The unit vectors \( \mathbf{t}_1, \mathbf{t}_2, \mathbf{n} \) are parallel to the co-ordinate lines and in the directions of increase of \( \xi_1, \xi_2, n \), respectively.

We assume the origins of the Eulerian and intrinsic coordinate systems are \( O \) and \( O' \), \( \mathbf{x} \) is the position vector of a point \( P \) in space relative to \( O \), and \( \mathbf{X} \) is the position vector relative to \( O \) of the projection of \( P \) onto \( \Gamma \) in the direction of the unit
normal $n$. Thus, we have $t_1 = \frac{\partial x}{\partial \xi_1}$, $t_2 = \frac{\partial x}{\partial \xi_2}$, $n = t_1 \times t_2$ and the following representation of the point $x$:

$$x = X(\xi_1, \xi_2, t) + n n(\xi_1, \xi_2, t), \quad (2.105)$$

where $X(\xi_1, \xi_2, t)$ represents the surface $\Gamma$. The change in the position vector $x$ corresponding to increments in $\xi_1, \xi_2, n$ and can be written as

$$dx = h_1 d\xi_1 t_1 + h_2 d\xi_2 t_2 + dn n, \quad (2.106)$$

where $h_1, h_2$ are functions of the coordinates, $h_i = \left| \frac{\partial x}{\partial \xi_i} \right| (1 + n \kappa_i)(i = 1, 2)$, and $\kappa_i$ are the principal curvatures of $\Gamma$ which also satisfy $\frac{\partial n}{\partial \xi_i} = \kappa_i \frac{\partial x}{\partial \xi_i}$.

Our next goal is to transform the time derivative in the Eulerian frame to the derivative in the moving frame with intrinsic coordinates fixed:

$$\frac{\partial}{\partial t} \bigg|_x = \frac{\partial}{\partial t} \bigg|_{\xi} - U_s \cdot \nabla_t + \frac{\partial n}{\partial t} \cdot \frac{\partial}{\partial n}, \quad (2.107)$$

here $U_s$ is the velocity of $O'$ relative to $O$ projected onto the tangent plane at $P$, $\nabla_t$ is the tangential gradient $\nabla_t = \frac{1}{h_1} \frac{\partial}{\partial \xi_1} t_1 + \frac{1}{h_2} \frac{\partial}{\partial \xi_2} t_2$, where $\nabla = \nabla_t + n \frac{\partial}{\partial n}$, and $\frac{\partial n}{\partial t} = -u_n$, where $u_n$ is normal speed of the surface $\Gamma$ relative to $O$ in the direction of $n$.

The fluid velocity $u$ can be decomposed into its projection $u_t$ onto the tangent plane and component $u_p$ in the normal direction, $u = u_t + u_p n$. Then $u \cdot \nabla = u_t \cdot \nabla_t + u_p \frac{\partial}{\partial n}$. If we let $v_p = u_p - u_n$ be the normal velocity of fluid relative to $\Gamma$ in intrinsic frame, and $v_t = u_t - U_s$ be the fluid velocity relative to $O'$ projected onto the tangent plane at $P$, then we can transform the material derivative as:

$$\frac{D}{Dt} = \frac{\partial}{\partial t} + u \cdot \nabla = \frac{\partial}{\partial t} + v_t \cdot \nabla_t + v_p \frac{\partial}{\partial n}. \quad (2.108)$$
By the transformation, the electrokinetic equations in the interface-attached intrinsic frame are then

\[
\begin{align*}
\frac{\partial n_+}{\partial t} \bigg|_\xi + v_{t+} \cdot \nabla_t n_+ + v_{p+} \frac{\partial n_+}{\partial n} + \nabla_I \cdot (\mp b_+ e n_+ \nabla_I \phi_+ - k_B T b_+ \nabla_I n_+) &= 0, \\
\frac{\partial n_-}{\partial t} \bigg|_\xi + v_{t-} \cdot \nabla_t n_- + v_{p-} \frac{\partial n_-}{\partial n} + \nabla_I \cdot (\mp b_- e n_- \nabla_I \phi_- - k_B T b_- \nabla_I n_-) &= 0.
\end{align*}
\]

(2.109)

In above equations, all operators are written in intrinsic coordinates, where, the form of \(\nabla_I = \nabla_t + n \frac{\partial}{\partial n}\) and \(\nabla_I^2\) is the Laplacian in intrinsic coordinates. We do not give all details of \(\nabla_I^2\), since, after rescaling the dimensionless equations, we only need the normal component in a leading order analysis.

2.5.2 Nondimensionalization

We consider time scale on the order of the charging time and solve the quasi-steady state problem. The scalings for both \(+\) and \(-\) regions are listed below:

\[
t = \frac{\lambda \rho L_0}{D_0}, \quad r = L_0 \tilde{r}, \quad \phi_\pm = \Phi_0 \tilde{\phi}_\pm, \quad u_\pm = U \tilde{u}_\pm, \quad n_\pm = n_0 \tilde{n}_\pm.
\]

(2.111)

The dimensionless ion density equations for \(+\) and \(-\) regions are (dropping tildes for simplicity)

\[
\begin{align*}
\frac{1}{\epsilon} \frac{\partial n_+}{\partial t} \bigg|_\xi + Pe \left( v_{t+} \cdot \nabla_t n_+ + v_{p+} \frac{\partial n_+}{\partial n} \right) + \nabla_I \cdot (\mp \Psi n_+ \nabla_I \phi_+ - \nabla_I n_+^\pm) &= 0, \\
\frac{1}{\epsilon} \frac{\partial n_-}{\partial t} \bigg|_\xi + \lambda Pe \left( v_{t-} \cdot \nabla_t n_- + v_{p-} \frac{\partial n_-}{\partial n} \right) + \nabla_I \cdot (\mp \Psi n_- \nabla_I \phi_- - \nabla_I n_-^\pm) &= 0.
\end{align*}
\]

(2.112)

(2.113)
The assumption that both Debye lengths are the same \((\epsilon_+ = \epsilon_-)\) is made here, which leads the equivalent relation for parameters \(\frac{K\lambda}{\alpha} = 1\). 

\[(2.114)\]

We rescale the normal direction \(n = \epsilon N\). For \(Pe = O(1)\), the leading order versions of (2.112, 2.113) are (for \('+\) and \('-\) regions)

\[
\frac{\partial}{\partial N}(\mp \Psi n_0^{(\pm)} \frac{\partial \phi_+}{\partial N} - \frac{\partial n^{(\pm)}_+}{\partial N}) = 0, 
\]

\[
\frac{\partial}{\partial N}(\mp \Psi n_0^{(\pm)} \frac{\partial \phi_-}{\partial N} - \frac{\partial n^{(\pm)}_-}{\partial N}) = 0. 
\]

\[(2.115)\]

\[(2.116)\]

The dimensionless no-flux boundary conditions for \('+\) and \('-\) regions at the interface \(N = 0\) are

\[
\mp \Psi n_0^{(\pm)} \frac{\partial \phi_+}{\partial N} - \frac{\partial n^{(\pm)}_+}{\partial N} = 0, 
\]

\[
\mp \Psi n_0^{(\pm)} \frac{\partial \phi_-}{\partial N} - \frac{\partial n^{(\pm)}_-}{\partial N} = 0. 
\]

\[(2.117)\]

\[(2.118)\]

The continuity of electric potential and the continuity of normal displacement at the interface \(N = 0\) are

\[
\phi_+ = \phi_-, 
\]

\[
\frac{\partial \phi_+}{\partial N} = -\alpha \frac{\partial \phi_-}{\partial N}. 
\]

\[(2.119)\]

\[(2.120)\]

Integrating the Equations (2.115) and (2.116) once, with the no-flux conditions (2.117) and (2.118) to determine the constants, we then integrate the equations again with far field boundary conditions for ion concentrations \(n^{(\pm)}_+(N \to \infty) = 1\) and \(n^{(\pm)}_-(N \to \infty) = \frac{n^{(0)}_-}{n^{(0)}_+} = K\lambda\) to obtain the solutions

\[
n_+^{(\pm)} = \exp(\mp \Psi(\phi_+ - \phi_{f+})), 
\]

\[
n_-^{(\pm)} = \frac{n^{(0)}_-}{n^{(0)}_+} \exp(\mp \Psi(\phi_- - \phi_{f-})). 
\]

\[(2.121)\]

\[(2.122)\]
with the far-field boundary condition \( \phi_{f\pm} = \phi_{\pm}(N \to \infty) \), which we can get from solving the outer problem.

The dimensionless Poisson’s equations are

\[
\epsilon^2 \nabla I^2 \phi_+ = -\frac{(n_+^{(+)}) - n_+^{(-)})}{2}, \tag{2.123}
\]
\[
\epsilon^2 \nabla I^2 \phi_- = -\frac{1}{\alpha} \frac{(n_-^{(+)}) - n_-^{(-)})}{2}, \tag{2.124}
\]

with solutions (2.121) and (2.122), the above equations become Poisson-Boltzmann equations

\[
\epsilon^2 \nabla I^2 \phi_+ = \sinh[\Psi(\phi_+ - \phi_{f+})], \tag{2.125}
\]
\[
\epsilon^2 \nabla I^2 \phi_- = \sinh[\Psi(\phi_- - \phi_{f-})]. \tag{2.126}
\]

Rescale \( n = \epsilon N \) and note the equations for the \( O(1) \) term are

\[
\Psi \frac{\partial^2 \phi_\pm}{\partial N^2} = \sinh[\Psi(\phi_\pm - \phi_{f\pm})]. \tag{2.127}
\]

This equation can be solved for both ‘\( \pm \)’ regions with boundary conditions (2.119) and (2.120). As a consistency check, we compare the solution of this equation with the steady state solution in Section 2.4 for the case \( \Psi \ll 1 \). After linearizing equation (2.127), we have

\[
\frac{\partial^2 \phi_\pm}{\partial N^2} = \phi_\pm - \phi_{f\pm}. \tag{2.128}
\]

We solve the equations and obtain:

\[
\phi_+ = -\frac{3\alpha}{2(1+\alpha)}E_\infty \cos \theta e^{-N} + \frac{3}{2} E_\infty \cos \theta, \tag{2.129}
\]
\[
\phi_- = \frac{3}{2(1+\alpha)}E_\infty \cos \theta e^{-N}, \tag{2.130}
\]

which are the same as the leading order steady state solutions in Section 2.4 for the drop with spherical shape. The exact solution of (2.127) with boundary conditions
Figure 2.4 The potential along the normal direction $\theta = 0$ with $E_\infty = 1$, and $K = 1$. The numerical solution (diamonds) of (2.127) are compared to the analytical solution for two different $\Psi$. The figure shows that electric potential goes down very steeply near the interface ($N = 0$) and changes very slowly for large $N$.

(2.119) and (2.120) can also be obtained by first computing the interfacial potential $\phi_s$,

$$\phi_s = \frac{1}{\Psi} \ln \frac{\alpha^2 - 1 - \alpha(e^{\Psi (\phi_f - \phi_s)} - e^{\Psi (\phi_s - \phi_f)})}{\alpha^2 e^{-\Psi \phi_f} - e^{-\Psi \phi_s}},$$  \hspace{1cm} (2.131)

here $\phi_{f\pm} = \phi_\pm (N \to \infty)$, then the exact solutions of (2.111) are

$$\phi_{\pm} = \frac{2}{\Psi} \ln \frac{1 + \tanh \left( \frac{\psi (\phi_s - \phi_{f\pm})}{4} \right) e^{-N}}{1 - \tanh \left( \frac{\psi (\phi_s - \phi_{f\pm})}{4} \right) e^{-N}} + \phi_{f\pm}.$$  \hspace{1cm} (2.132)

We have also solved 1-D Poisson-Boltzmann equations (2.127) numerically and compared it with the exact solutions above, with the results illustrated by Figure 2.4. For the numerical solution, we use a spectral method to compute the second derivative via $D_N^2$ ($D_N$ is the Chebyshev differentiation matrix here), then we solve the nonlinear
equation by Newton’s method with quadratic convergence. The numerical simulation shows that there is a steep decline near the interface.

We have presented the numerical solutions for the electric field and given the leading order analytic solutions for charge density and potential. In next chapter, we consider the fluid flow due to the effect of the electric force.
CHAPTER 3

FLUID DYNAMICS

To determine the drop deformation in fluid flow that is induced by the applied electric field, we need to calculate the velocity by solving Stokes equation. In this chapter, the problem is formulated by considering both electric and osmotic stress. The electric stress comes from the Maxwell stress tensor and can be calculated as

$$F_E = qE = -e(n^+ - n^-)\nabla \phi = \varepsilon \nabla (\phi_\infty + \eta) \nabla^2 (\phi_\infty + \eta) = \varepsilon \nabla (\phi_\infty + \eta) \nabla^2 \eta, \quad (3.1)$$

where we have used Poisson's equation $\nabla^2 \phi = -e(n^+ - n^-)/\varepsilon$ to replace $e(n^+ - n^-)$ (note that $\nabla^2 \phi_\infty = 0$). The potential $\phi$ here is total potential which is decomposed as $\phi = \phi_o + \eta$, where $\phi_o = \lim_{N \to \infty} \phi$, and $\eta$ is the excess potential.

The osmotic stress comes from the gradient of ion concentration, and using the result $n^{(\pm)} = n^{(0)} \exp(\pm \Psi_F \Phi_0 (\phi - \phi_o))$, the osmotic stress can be expressed as

$$F_o = -k_B T \nabla (n^+ + n^-) = k_B T \Psi_F \Phi_0 (n^+ - n^-) \nabla \eta = e(n^+ - n^-) \nabla \eta = -\varepsilon \nabla \eta \nabla^2 \eta. \quad (3.2)$$

The total stress is obtained from adding (3.1) and (3.2)

$$F = F_E + F_o = \varepsilon \nabla \phi_o \nabla^2 \eta, \quad (3.3)$$

which is used as body force in the Stokes equation

$$\mu \nabla^2 u - \nabla P = -\varepsilon \nabla^2 \eta \nabla \phi_o. \quad (3.4)$$

Before analyzing the fluid dynamics both inside and outside the drop, we need to derive the dimensionless equations. We define dimensionless variables $\tilde{\phi}, \tilde{\eta}, etc.$ by

$$\phi = \Phi_o \tilde{\phi}, \; \eta = \Phi_o \tilde{\eta}, \; u = U \tilde{u}, \; x = L_o \tilde{x}, \; P = \frac{\mu U}{L_o} \tilde{P}. \quad (3.5)$$
The subscript ‘+’ denotes quantities in the outer fluid, which are used in the nondimensionalization. It is also convenient to write the Helmholtz-Smoluchowski slip velocity using the potential $\phi_o$ as

$$U = \frac{\varepsilon_+ \phi^2}{L_0 \mu_+} = \frac{\varepsilon_+ E^2_\infty}{\mu_+}. \quad (3.6)$$

The variables (3.5) are substituted into equation (3.4) to obtain (dropping tildes)

$$\nabla^2 u_+ - \nabla P_+ = -\nabla^2 \eta_+ \nabla \phi_{o+}, \quad (3.7)$$

$$\lambda \nabla^2 u_- - \nabla P_- = -\alpha \nabla^2 \eta_- \nabla \phi_{o-}, \quad (3.8)$$

where $\lambda = \frac{\mu_-}{\mu_+}$, $\alpha = \frac{\varepsilon_-}{\varepsilon_+}$.

The boundary condition at the drop interface is a balance of electric stress, osmotic stress, fluid stress and surface tension

$$[(T_M + T_O + T_H) \cdot n]^+ = 2\kappa \gamma n, \quad (3.9)$$

where

$$T_{Mij} = \varepsilon [E_i E_j - \frac{1}{2} \delta_{ij} (\mathbf{E} \cdot \mathbf{E})] = \varepsilon [\partial_{x_i} \phi \partial_{x_j} \phi - \frac{1}{2} \delta_{ij} (\partial_{x_k} \phi \cdot \partial_{x_k} \phi)], \quad (3.10)$$

$$T_{Oij} = -\varepsilon [\partial_{x_i} \eta \partial_{x_j} \eta - \frac{1}{2} \delta_{ij} (\partial_{x_k} \eta \cdot \partial_{x_k} \eta)] \quad (3.11)$$

are the Maxwell and osmotic stress tensors, $[f]^+ = f_+ - f_-$ denotes the jump of $f$ across the interface, $\kappa$ is the local mean curvature of the surface and $\gamma$ is the interface tension. Note that $F_O = \nabla \cdot T_O$ and $F_E = \nabla \cdot T_M$.

The stress balance equation is made dimensionless using the scales (3.5), along with $\kappa = \frac{\kappa}{L_0}$. We get (dropping tildes)

$$[(T_M + T_O + T_H) \cdot n]^+ = \frac{2\kappa n}{Ca}, \quad (3.12)$$
where

\[ Ca = \frac{\mu U}{\gamma} \]  \hspace{1cm} (3.13)

is the electric capillary number.
CHAPTER 4

BOUNDARY INTEGRAL METHOD

4.1 Introduction

We develop a boundary integral representation involving the boundary values of the velocities and surface force, taking into consideration slip velocities caused by the Debye layers both inside and outside the drop. It is convenient to start from the Lorentz reciprocal identity, see [25]’s analysis for classical boundary integral equation.

4.2 Lorentz Reciprocal Identity

We consider the Stokes equation in Newtonian flow. The stress tensor $\sigma$ can be written as:

$$\sigma_{ij} = -\delta_{ij}P + \mu \left( \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right). \tag{4.1}$$

For any two nonsingular (regular) flows $u$ and $u'$ with corresponding stress tensors $\sigma$ and $\sigma'$, we have

$$\frac{\partial}{\partial x_k} (u'_i \sigma_{ik} - u_i \sigma'_{ik}) = 0. \tag{4.2}$$

4.3 Boundary Integral Representation

Identifying $u'$ with the flow due to a point force with arbitrary strength $g$ located at the point $x_0$, we obtain

$$u'_i = \frac{1}{8\pi \mu} G_{ij}(x, x_0) g_j, \quad \sigma'_{ik} = \frac{1}{8\pi} T_{ijk}(x, x_0) g_j. \tag{4.3}$$

Plugging (4.3) into (4.2) with arbitrary constant $g$, we obtain

$$\frac{\partial}{\partial x_k} [G_{ij}(x, x_0) \sigma_{ik}(x) - \mu u_i(x) T_{ijk}(x, x_0)] = 0. \tag{4.4}$$
Consider a particle of fluid of viscosity $\mu_2$ (fluid 2) inside a fluid of viscosity $\mu_1$ (fluid 1). $V$ is the exterior (fluid 1) fluid domain, $S$ is the boundary (shown in Figure 4.1), $\mu_2$ can be infinite, in which case fluid 2 is a solid particle.

**Figure 4.1** Fluid domain $V$ with boundary $S$, when $x_0 \in V$.

From Lorentz reciprocal theorem, for a point $x_0$ outside of $V$ (i.e., in fluid 2 or the exterior of $V$), noting that the function within the square bracket in (4.4) is regular throughout $V$, integrating (4.4) over $V$, with using the divergence theorem, we obtain

$$\int_S [G_{ij}(x, x_0)\sigma_{ik}(x) - \mu_1 u_i(x)T_{ijk}(x, x_0)]n_k(x)dS(x) = 0. \quad (4.5)$$

For a point $x_0 \in V$, i.e., $x_0$ is in fluid 1 (Figure 4.1), with the analysis about a small spherical volume $V_\epsilon$ of radius $\epsilon$ centered at $x_0$ ([25]), we can obtain the desired
boundary integral representation in the term of integration over the surface $S$:

$$u_j(x_0) = -\frac{1}{8\pi \mu_1} \int_S \sigma_{ik}(x)n_k(x)G_{ij}(x,x_0)dS(x) + \frac{1}{8\pi} \int_S u_i(x) T_{ijk}(x,x_0)n_k(x)dS(x).$$

(4.6)

### 4.4 Interfacial Flow

The goal is to obtain the boundary integral formulation for the flow due to interfaces. We use standard boundary integral equations from the previous section. The case with a droplet is considered here. Let $V_+$ and $V_-$ represent the exterior and interior of the drop. Let the outer boundary of $S$ tend to $\infty$ and assume the flow vanishes at $\infty$. The interface of the droplet is the boundary $S$ now.

We separate this section into three parts. In Part 1, we evaluate the integrals with a point $x_0 \in V_+$, while in Part 2, we evaluate the integrals with a point $x_0 \in V_-$. Finally, we combine results from Part 1 and Part 2 by approaching $x_0$ to the interface from the internal and external side.

#### 4.4.1 Part 1: $x_0 \in V_+$

Now, we select a point $x_0$ in $V_+$, evaluating the integrand of (4.4) over volume $V_+$, we obtain the representation for the velocity of $x_0$ from (4.6)

$$u_j(x_0) = -\frac{1}{8\pi \mu_+} \int_S f^+_i(x)G_{ij}(x,x_0)dS(x) + \frac{1}{8\pi} \int_S u^+_i(x) T_{ijk}(x,x_0)n_k(x)dS(x),$$

(4.7)

where $f^+$ denotes the force outside the Debye layer in the exterior $V_+$. This is different from the classical model, where $f$ denotes the interfacial surface force in the exterior. $u^+$ denotes the velocity outside of the Debye layer in the exterior $V_+$, which is the combination of interfacial velocity and slip velocity. $\mu_+$ denotes the viscosity in $V_+$.

Then, evaluating the integrand over $V_-$, we obtain the representation from (4.5)

$$\int_S f^-_i G_{ij}(x,x_0)dS(x) - \mu_\int_S u^-_i(x) T_{ijk}(x,x_0)n_k(x)dS(x) = 0,$$

(4.8)
where \( f^- \) and \( u^- \) denote the force and velocity outside the Debye layer in the interior \( V_- \), \( \mu_- \) is the viscosity in \( V_- \). We multiply (4.8) by \( \frac{1}{8\pi \mu_+} \) and combine it with (4.7) to obtain

\[
\begin{align*}
    u_j^+(x_0) &= -\frac{1}{8\pi \mu_+} \int_S [f_i^+ - f_i^-](x)G_{ij}(x,x_0)dS(x) \\
    &\quad + \frac{1}{8\pi} \int_S [u_i^+(x) - \frac{\mu_-}{\mu_+} u_i^-(x)]T_{ijk}(x,x_0)n_k(x)dS(x),
\end{align*}
\]

The fluid velocity outside the Debye layer can be expressed by combining the interfacial velocity \( u^I \) and the slip velocity \( u^S \), which is given from inner problem. Thus, we have the following equations:

\[
\begin{align*}
    u_i^+ &= u_i^I + u_i^{S+}, \\
    u_i^- &= u_i^I + u_i^{S-},
\end{align*}
\]

where \( u_i^I \) is \( i^{th} \) component of the interface velocity, i.e., \( u_i^I = x_t \cdot e_i \) with \( x \) be the position vector of the interface which is a function of \( \xi_1, \xi_2, \xi_3 \) and time \( t \). \( \xi_1, \xi_2 \) and \( \xi_3 \) are surface-fitted orthogonal coordinates which will be introduced in next chapter.
Furthermore, we shall denote the viscosity ratio between the internal and the external fluid by $\lambda = \frac{\mu_+}{\mu_-}$, and rewrite (4.9) as

$$u^+_j(x_0) = -\frac{1}{8\pi\mu_+} \int_S [f^+_i - f^-_i](x)G_{ij}(x, x_0)dS(x)$$
$$+ \frac{1 - \lambda}{8\pi} \int_S u'_i(x)T_{ijk}(x, x_0)n_k(x)dS(x)$$
$$+ \frac{1}{8\pi} \int_S u'^+_i(x)T_{ijk}(x, x_0)n_k(x)dS(x) - \frac{\lambda}{8\pi} \int_S u'^-_i(x)T_{ijk}(x, x_0)n_k(x)dS(x).$$

(4.12)

Now, letting $x_0$ approach the interface from the external side, we have

$$u^+_j(x_0) = u'_j(x_0) + u'^+_j(x_0).$$

(4.13)

4.4.2 Part 2: $x_0 \in V_-$

![Diagram](image)

Figure 4.3 $x_0 \in V_-$

Now, we select a point $x_0$ in $V_-$, evaluating the integrand of (4.4) over volume $V_+$, we obtain the representation for the velocity of $x_0$ from (4.5)

$$\int_S f^+_i G_{ij}(x, x_0)dS(x) - \mu_+ \int_S u'^+_i(x)T_{ijk}(x, x_0)n_k(x)dS(x) = 0,$$

(4.14)
then, evaluating the integrand over $V_-$, we obtain the representation from (4.6)

$$u^\tau_j(x_0) = \frac{1}{8\pi\mu_-} \int_S f_i^\tau(x) G_{ij}(x, x_0) dS(x) - \frac{1}{8\pi} \int_S u^\tau_i(x) T_{ijk}(x, x_0) n_k(x) dS(x).$$

(4.15)

We multiply (4.14) by $-\frac{1}{8\pi\mu_-}$ and combine it with (4.15) to obtain

$$u^\tau_j(x_0) = -\frac{1}{8\pi\mu_-} \int_S [f^+_i - f^-_i](x) G_{ij}(x, x_0) dS(x) + \frac{1}{8\pi} \int_S u'^+_i(x) T_{ijk}(x, x_0) n_k(x) dS(x) + \frac{1}{8\pi} \int_S u'^-_i(x) T_{ijk}(x, x_0) n_k(x) dS(x).$$

(4.16)

Now, letting $x_0$ approach the interface from the internal side, we have

$$u^\tau_j(x_0) = u'^+_j(x_0) + u'^-_j(x_0).$$

(4.17)

4.4.3 Combination

Before combining (4.12) and (4.16), we consider the behavior of the double layer potential. Applying the boundary integral equation for the flow in the exterior and interior of the drop, considering the limit as the field point $x_0$ approaches $S$ from either side, we obtain

$$\int_S u^+_i(x) T_{ijk}(x, x_0) n_k(x) dS(x) = \int_S^{P.V.} u^+_i(x) T_{ijk}(x, x_0) n_k(x) dS(x) - 4\pi u^+_j(x_0),$$

(4.18)

$$\int_S u^-_i(x) T_{ijk}(x, x_0) n_k(x) dS(x) = \int_S^{P.V.} u^-_i(x) T_{ijk}(x, x_0) n_k(x) dS(x) + 4\pi u^-_j(x_0),$$

(4.19)

where $\int^{P.V.}$ denotes the principal value of the integral. These two equations can be applied into (4.12) and (4.16) to get

$$u'^+_j(x_0) + u'^+_j(x_0) = -\frac{1}{8\pi\mu_+} \int_S [f_i^\tau_i(x) G_{ij}(x, x_0) dS(x)$$
\[ u^I_j(x_0) + u^S_j(x_0) = -\frac{1}{8\pi\mu} \int_S [f_i]^+(x)G_{ij}(x, x_0) dS(x) \]
\[ + \frac{1 - \lambda}{8\pi} \int_S u^I_i(x) T_{ijk}(x, x_0) n_k(x) dS(x) - \frac{1}{2} u^I_j(x_0) \]
\[ - \frac{\lambda}{8\pi} \int_S u^S_i(x) T_{ijk}(x, x_0) n_k(x) dS(x) + \frac{\lambda}{2} u^S_j(x_0), \quad (4.20) \]

where \([f_i]^+ = f_i^+ - f_i^-\) is the discontinuity in the force, which needs to be analyzed from stress balance equation and inner problems. Then we compute \((4.20) + (4.21) \times \lambda\) to get the final boundary integral formulation

\[ u^I_j(x_0) = -\frac{1}{4\pi\mu + (1 + \lambda)} \int_S [f_i]^+(x)G_{ij}(x, x_0) dS(x) \]
\[ + \frac{1 - \lambda}{4\pi(1 + \lambda)} \int_S u^I_i(x) T_{ijk}(x, x_0) n_k(x) dS(x) \]
\[ - \frac{1}{1 + \lambda} u^S_j(x_0) - \frac{\lambda}{1 + \lambda} u^S_j(x_0) \]
\[ + \frac{1}{4\pi(1 + \lambda)} \int_S u^S_i(x) T_{ijk}(x, x_0) n_k(x) dS(x) \
\[ - \frac{\lambda}{4\pi(1 + \lambda)} \int_S u^S_i(x) T_{ijk}(x, x_0) n_k(x) dS(x). \quad (4.22) \]

For classical boundary integral representation, there is no slip velocity, which means \(u^{S\pm} = 0\). Then, we only have the first two terms of the right hand side of the above equation, which is the same as the classical BIE.
4.5 Nondimensionalization

In order to compute with dimensionless BIE and match the scales used for slip velocities and stress tensors, we use the scales as following:

\[ u = U \tilde{u}, \quad f = f_0 \tilde{f}, \quad x = L_0 \tilde{x}, \quad G = \frac{1}{L_0} \tilde{G}, \quad T = \frac{1}{L_0^2} \tilde{T}. \] (4.23)

From the matched scales in stress balance equation in next chapter, we have

\[ U = \frac{\varepsilon + E_\infty^2 L_0}{\mu_+}, \quad f_0 = \varepsilon + E_\infty^2. \] (4.24)

Thus, the dimensionless boundary integral equation is (dropping tildes)

\[
\begin{align*}
    u_j^L(x_0) &= - \frac{1}{4\pi(1 + \lambda)} \int_S \left[ f_i^+(x)G_{ij}(x, x_0) - \frac{1 - \lambda}{1 + \lambda} \int_{P.V.} u_i^L(x)T_{ijk}(x, x_0)n_k(x) dS(x) \right] dS(x) \\
    &\quad + \frac{1}{4\pi(1 + \lambda)} \int_{P.V.} u_i^L(x)T_{ijk}(x, x_0)n_k(x) dS(x) - \frac{\lambda}{4\pi(1 + \lambda)} \int_{P.V.} u_i^S(x)T_{ijk}(x, x_0)n_k(x) dS(x) \\
    &\quad - \frac{\lambda}{4\pi(1 + \lambda)} \int_{P.V.} u_i^S(x)T_{ijk}(x, x_0)n_k(x) dS(x).
\end{align*}
\] (4.25)
5.1 Introduction

Our goal is to compute the jump in traction $[T_{Ho} \cdot n]^\pm$ which is used in our boundary integral representation, here $[ \ ]^\pm$ means the jump from '$+$ region to '$-$ region, $T_{Ho\pm}$ means the hydrodynamic stress tensor in the Debye layer as the scaled normal direction $N \to \infty$, as Figure 5.1 shows.

Figure 5.1 Notations for different stress tensors
Our strategy is to calculate the stress jump \([T_H \cdot \mathbf{n}]^+\) first, where \(T_{H \pm}\) is the hydrodynamic stress tensor in the Debye layer at \(N = 0\), then we compute the difference between \(T_{Ho} \cdot \mathbf{n}\) and \(T_H \cdot \mathbf{n}\) in both regions, finally we can get

\[
[T_{Ho} \cdot \mathbf{n}]^+ = [T_H \cdot \mathbf{n}]^+ + (T_{Ho+} \cdot \mathbf{n} - T_{H+} \cdot \mathbf{n}) - (T_{Ho-} \cdot \mathbf{n} - T_{H-} \cdot \mathbf{n}).
\] (5.1)

### 5.2 Dimensional Stress Balance Equation

We have the dimensional stress balance equation across the interface \((N = 0)\), which is

\[
[(T_M + T_O + T_H) \cdot \mathbf{n}]^+ = 2\kappa\gamma\mathbf{n},
\] (5.2)

where \(T_M, T_O\) and \(T_H\) are Maxwell, osmotic and hydrodynamic stress tensor, \(\kappa\) is the local mean curvature of the surface and \(\gamma\) is the interface tension.

The potential \(\phi\) here is total potential which is decomposed as \(\phi = \phi_\infty + \eta\), where \(\phi_\infty = \lim_{N \to \infty} \phi\), and \(\eta\) is the excess potential. Then the Maxwell and osmotic stress tensors in local Cartesian co-ordinates are

\[
T_{M\pm ij} = \varepsilon_\pm [\partial_{x_i} \phi_\pm \partial_{x_j} \phi_\pm - \frac{1}{2}\delta_{ij} (\partial_{x_k} \phi_\pm \cdot \partial_{x_k} \phi_\pm)],
\] (5.3)

\[
T_{O\pm ij} = -\varepsilon_\pm [\partial_{x_i} \eta_\pm \partial_{x_j} \eta_\pm - \frac{1}{2}\delta_{ij} (\partial_{x_k} \eta_\pm \cdot \partial_{x_k} \eta_\pm)].
\] (5.4)

### 5.3 Nondimensionalization

The scales for nondimensionalization are

\[
\phi = \Phi_\phi \tilde{\phi}, \quad \eta = \Phi_\eta \tilde{\eta}, \quad \mathbf{u} = U \tilde{\mathbf{u}}, \quad \mathbf{x} = L_0 \tilde{\mathbf{x}}, \quad P = \frac{\mu_+ U}{L_0 \tilde{P}}.
\] (5.5)

The subscript ‘+’ denotes quantities in the outer fluid, which are used in the nondimensionalization. It is also convenient to write the Helmholtz-Smoluchowski
slip velocity using the potential $\Phi_0$ as

$$U = \frac{\varepsilon_+ \Phi_0^2}{L_0 \mu_+} = \frac{\varepsilon_+ E_\infty^2 L_0}{\mu_+}.$$  \hfill (5.6)

Let

$$\kappa = \frac{\bar{\kappa}}{L_0}, \ C_a = \frac{\mu_+ U}{\gamma}, \ \alpha = \frac{\varepsilon_-}{\varepsilon_+}, \ \lambda = \frac{\mu_-}{\mu_+},$$  \hfill (5.7)

then the dimensionless stress balance equation becomes (dropping tildes)

$$(T_{M+} + T_{O+}) \cdot \mathbf{n} - \alpha(T_{M-} + T_{O-}) \cdot \mathbf{n} + (T_{H+} \cdot \mathbf{n} - T_{H-} \cdot \mathbf{n}) = \frac{2\kappa n}{C_a},$$  \hfill (5.8)

where

$$T_{M\pm ij} = \partial_{x_i} \phi_{\pm} \partial_{x_j} \phi_{\pm} - \frac{1}{2} \delta_{ij} (\partial_{x_k} \phi_{\pm} \cdot \partial_{x_k} \phi_{\pm}),$$  \hfill (5.9)

$$T_{O\pm ij} = -\partial_{x_i} \eta_{\pm} \partial_{x_j} \eta_{\pm} - \frac{1}{2} \delta_{ij} (\partial_{x_k} \eta_{\pm} \cdot \partial_{x_k} \eta_{\pm}),$$  \hfill (5.10)

and

$$T_{H+ij} = -P\sigma_{ij} + (\partial_{x_i} u_i + \partial_{x_j} u_j),$$  \hfill (5.11)

$$T_{H-ij} = -P\sigma_{ij} + \lambda (\partial_{x_i} u_i + \partial_{x_j} u_j).$$  \hfill (5.12)

Next step, we write

$$[T_H \cdot \mathbf{n}]^+ = \frac{2\kappa n}{C_a} \left[ (T_{M+} + T_{O+}) \cdot \mathbf{n} - \alpha(T_{M-} + T_{O-}) \cdot \mathbf{n} \right].$$  \hfill (5.13)

### 5.4 Obtain the Leading Order Terms in Intrinsic Surface Coordinates

The general 3-D model will be discussed here for the stokes equations before we choose the specific axisymmetric case to obtain the solutions in our model. Let the drop surface be $S$, we need to form an inner region expansion for inner variables in $\epsilon$. Thus, at a general completely point $O$ on the surface $S$ we define a set of local orthogonal curvilinear coordinates $(\xi_1, \xi_2, \xi_3)$ attached to the moving lines, and the
unit vectors \( \mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3 \) are parallel to the co-ordinate lines and in the directions of increase of \( \xi_1, \xi_2, \xi_3 \), respectively. \( (\xi_1, \xi_2) \) are lying within the surface \( S \) with unit metric tensor in terms of the outer variables. At \( O \) we also define local Cartesian coordinates \( (x, y, z) \) with \( z \) normal to \( S \) and directed into the outer fluid, \( x- \) and \( y- \) axes tangent to the \( \xi_1 \) and \( \xi_2 \) coordinate lines at \( O \).

In an interface based co-ordinates, the velocity of the surface at \( O \) adopts the form

\[
\mathbf{U} = U\mathbf{e}_1 + V\mathbf{e}_2 + W\mathbf{e}_3,
\]

(5.14)

where \( \mathbf{e}_1, \mathbf{e}_2 \) and \( \mathbf{e}_3 \) are expressed later. And inner velocity \( \mathbf{u} \) which is the inner region variable is written as

\[
\mathbf{u} = u\mathbf{e}_1 + v\mathbf{e}_2 + w\mathbf{e}_3,
\]

(5.15)

it is defined as

\[
\mathbf{v} = \mathbf{U} + \mathbf{u},
\]

(5.16)

where \( \mathbf{v} \) is the total velocity of fluid within the double layer.

We have the dimensionless Stokes equations for inner region fluid flow in ’+’ and ’−’ regions:

\[
\nabla^2 \mathbf{v}_+ - \nabla P_+ = -\nabla^2 \eta_+ \nabla \phi_o + ,
\]

(5.17)

\[
\lambda \nabla^2 \mathbf{v}_- - \nabla P_- = -\alpha \nabla^2 \eta_- \nabla \phi_o - ,
\]

(5.18)

with the incompressibility condition

\[
\nabla \cdot \mathbf{v}_\pm = 0.
\]

(5.19)

Let’s consider the first equation (drop ’+’):

\[
\nabla^2 (\mathbf{U} + \mathbf{u}) - \nabla P = -\nabla^2 \eta \nabla \phi_o .
\]

(5.20)
For the inner variables $u$, $P$, and $\eta$, we need to transform the operators $\nabla^2$ and $\nabla$ into the curvilinear coordinate system.

The change in the position vector $\mathbf{x}$ corresponding to increments in $\xi_1, \xi_2$ and $\xi_3$ can then be written as

$$d\mathbf{x} = l_1 d\xi_1 \mathbf{e}_1 + l_2 d\xi_2 \mathbf{e}_2 + l_3 d\xi_3 \mathbf{e}_3,$$

(5.21)

where $l_1, l_2$ and $l_3$ are functions of the coordinates, which will be defined later for chosen intrinsic coordinates. To find the component of $\nabla^2 u$ we use the identity

$$\nabla^2 u = \nabla (\nabla \cdot u) - \nabla \times (\nabla \times u).$$

(5.22)

Since we know

$$\nabla \cdot u = \frac{1}{l_1 l_2 l_3} \left[ \frac{\partial (l_2 l_3 u)}{\partial \xi_1} + \frac{\partial (l_3 l_1 v)}{\partial \xi_2} + \frac{\partial (l_1 l_2 w)}{\partial \xi_3} \right],$$

(5.23)

then

$$\nabla (\nabla \cdot u) = \frac{1}{l_1} \frac{\partial}{\partial \xi_1} \left\{ \frac{1}{l_1 l_2 l_3} \left[ \frac{\partial (l_2 l_3 u)}{\partial \xi_1} + \frac{\partial (l_3 l_1 v)}{\partial \xi_2} + \frac{\partial (l_1 l_2 w)}{\partial \xi_3} \right] \right\} \mathbf{e}_1 + \frac{1}{l_2} \frac{\partial}{\partial \xi_2} \left\{ \frac{1}{l_1 l_2 l_3} \left[ \frac{\partial (l_2 l_3 u)}{\partial \xi_1} + \frac{\partial (l_3 l_1 v)}{\partial \xi_2} + \frac{\partial (l_1 l_2 w)}{\partial \xi_3} \right] \right\} \mathbf{e}_2 + \frac{1}{l_3} \frac{\partial}{\partial \xi_3} \left\{ \frac{1}{l_1 l_2 l_3} \left[ \frac{\partial (l_2 l_3 u)}{\partial \xi_1} + \frac{\partial (l_3 l_1 v)}{\partial \xi_2} + \frac{\partial (l_1 l_2 w)}{\partial \xi_3} \right] \right\} \mathbf{e}_3,$$

(5.24)

And

$$\nabla \times u = \frac{1}{l_2 l_3} \left[ \frac{\partial (l_3 w)}{\partial \xi_2} - \frac{\partial (l_2 v)}{\partial \xi_3} \right] \mathbf{e}_1 + \frac{1}{l_1 l_3} \left[ \frac{\partial (l_1 u)}{\partial \xi_3} - \frac{\partial (l_3 w)}{\partial \xi_1} \right] \mathbf{e}_2 + \frac{1}{l_1 l_2} \left[ \frac{\partial (l_2 v)}{\partial \xi_1} - \frac{\partial (l_1 u)}{\partial \xi_2} \right] \mathbf{e}_3,$$

(5.25)

then

$$\nabla \times (\nabla \times u)$$
\[
\frac{1}{l_2 l_3} \left\{ \frac{\partial}{\partial \xi_2} \left[ l_3 \left( \frac{\partial (l_2 v)}{\partial \xi_1} - \frac{\partial (l_1 u)}{\partial \xi_2} \right) \right] - \frac{\partial}{\partial \xi_3} \left[ l_2 \left( \frac{\partial (l_1 u)}{\partial \xi_3} - \frac{\partial (l_3 w)}{\partial \xi_1} \right) \right] \right\} e_1
\]
\[
+ \frac{1}{l_1 l_3} \left\{ \frac{\partial}{\partial \xi_3} \left[ l_1 \left( \frac{\partial (l_3 w)}{\partial \xi_2} - \frac{\partial (l_2 v)}{\partial \xi_3} \right) \right] - \frac{\partial}{\partial \xi_1} \left[ l_3 \left( \frac{\partial (l_2 v)}{\partial \xi_1} - \frac{\partial (l_1 u)}{\partial \xi_2} \right) \right] \right\} e_2
\]
\[
+ \frac{1}{l_1 l_2} \left\{ \frac{\partial}{\partial \xi_1} \left[ l_2 \left( \frac{\partial (l_1 u)}{\partial \xi_3} - \frac{\partial (l_3 w)}{\partial \xi_1} \right) \right] - \frac{\partial}{\partial \xi_2} \left[ l_1 \left( \frac{\partial (l_3 w)}{\partial \xi_2} - \frac{\partial (l_2 v)}{\partial \xi_3} \right) \right] \right\} e_3.
\]

(5.26)

The gradient of \( P \) is
\[
\nabla P = \frac{1}{l_1} \frac{\partial P}{\partial \xi_1} e_1 + \frac{1}{l_2} \frac{\partial P}{\partial \xi_2} e_2 + \frac{1}{l_3} \frac{\partial P}{\partial \xi_3} e_3.
\]

(5.27)

And
\[
\nabla^2 \eta = \frac{1}{l_1 l_2 l_3} \left[ \frac{\partial}{\partial \xi_1} \left( l_2 l_3 \frac{\partial \eta}{\partial \xi_1} \right) + \frac{\partial}{\partial \xi_2} \left( l_3 l_1 \frac{\partial \eta}{\partial \xi_2} \right) + \frac{\partial}{\partial \xi_3} \left( l_1 l_2 \frac{\partial \eta}{\partial \xi_3} \right) \right].
\]

(5.28)

For the outer variable \( \phi_o \), let’s define
\[
-\nabla \phi_o = E_1 e_1 + E_2 e_2 + E_3 e_3.
\]

(5.29)

In the incompressibility condition, we transform the divergence operator for inner velocity \( u \) in equation \( \nabla \cdot (U + u) = 0 \) and have
\[
\nabla \cdot U + \frac{1}{l_1 l_2 l_3} \left[ \frac{\partial (l_2 l_3 u)}{\partial \xi_1} + \frac{\partial (l_3 l_1 v)}{\partial \xi_2} + \frac{\partial (l_1 l_2 w)}{\partial \xi_3} \right] = 0
\]

(5.30)

Now, the surface-fitted orthogonal coordinates are introduced, \( \xi_1 \) and \( \xi_2 \)–directions are aligned with the principal directions of curvature and \( \xi_3 = n \) is the distance along the normal measured from the surface \( S \). Then the unit vector \( e_3 = n = e_1 \times e_2 \), we can write the position vector \( x \) as
\[
x = \mathbf{X}(\xi_1, \xi_2, t) + n(\xi_1, \xi_2, t).
\]

(5.31)

Thus, the unit vectors satisfy
\[
e_i = \frac{1}{a_i \partial \xi_i} \nabla \mathbf{X},
\]

(5.32)
\[
\begin{align*}
\frac{\partial \mathbf{n}}{\partial \xi_i} &= \kappa_i \frac{\partial \mathbf{X}}{\partial \xi_i},
\end{align*}
\]

(5.33)

where \(i = 1, 2\), \(a_i = \left| \frac{\partial \mathbf{X}}{\partial \xi_i} \right|\) and \(\kappa_i\) are the principal curvatures of \(S\). Thus, we have

\[
\begin{align*}
l_i &= a_i(1 + n \kappa_i)(i = 1, 2), l_3 = 1.
\end{align*}
\]

(5.34)

For inner problems, we need to rescale \(n = \epsilon N\ (\epsilon = \lambda_D/L)\). In order to balance equation (5.30), we need to rescale \(w = \epsilon \tilde{w}\).

During the following analysis, the generic asymptotic series will be used to expand all fields:

\[
f(\xi_1, \xi_2, N; \epsilon) \sim f_0(\xi_1, \xi_2, N) + \epsilon f_1(\xi_1, \xi_2, N) + \ldots
\]

(5.35)

5.5 Leading Order Problem for the Third Component of Stokes Equation

Now we consider the third component of Stokes equation (5.20), the leading term (dropping tildes for convenience) is

\[
\frac{\partial}{\partial N} \left[ \frac{1}{l_1 l_2} \frac{\partial (l_1 l_2 w)}{\partial N} \right]
\]

(5.36)
in \(\nabla^2 (U + u)\). With the definitions of \(l_1, l_2\) in (5.34) and generic expansion of \(w\), the leading order \(O(\frac{\epsilon}{\epsilon})\) term coming from \(\nabla^2 (U + u)\) is

\[
\frac{\partial}{\partial N} \left[ \frac{1}{a_1 a_2} \frac{\partial (a_1 a_2 w_0)}{\partial N} \right]
\]

(5.37)

Similarly, the leading order \(O(\frac{\epsilon}{\epsilon})\) term coming from \(\nabla P\) is

\[
\frac{\partial P_0}{\partial N},
\]

(5.38)
since \(P_0\) should be matched with the outer solution which is \(O(1)\).

And the leading order \(O(\frac{1}{\epsilon})\) term coming from \(-\nabla^2 \eta \nabla \phi_o\) is 0, since the third component of \(\nabla \phi_o\) is 0 at the quasi-steady state for outer electric field.
The leading order equation becomes
\[
\frac{\partial P_0}{\partial N} = \frac{\partial}{\partial N} \left[ \frac{1}{a_1 a_2} \frac{\partial (a_1 a_2 w_0)}{\partial N} \right].
\] (5.39)

We apply the definitions of \(a_1, a_2\) into this equation to get the leading order equation for \(P_0\) and \(w_0\)
\[
\frac{\partial P_0}{\partial N} = \frac{\partial^2 w_0}{\partial N^2}.
\] (5.40)

The solution is
\[
P_0 = \frac{\partial w_0}{\partial N} + H(\xi_1, \xi_2),
\] (5.41)
then we have (with ‘+’)
\[
\left( P_{0+} - \frac{\partial w_{0+}}{\partial N} \right) \bigg|_{N=+\infty} = \left( P_{0+} - \frac{\partial w_{0+}}{\partial N} \right) \bigg|_{N=0} = H_{+}(\xi_1, \xi_2),
\] (5.42)
the similar solution for ‘−’ region can also be obtained
\[
\left( P_{0-} - \lambda \frac{\partial w_{0-}}{\partial N} \right) \bigg|_{N=+\infty} = \left( P_{0-} - \lambda \frac{\partial w_{0-}}{\partial N} \right) \bigg|_{N=0} = H_{-}(\xi_1, \xi_2),
\] (5.43)
where \(P_{0\pm}\) is \(N\)–dependent.

In the incompressibility condition (5.30), \(\nabla \cdot \mathbf{U}\) does not change as \(N\) varies within the layer, thus,
\[
\frac{1}{l_1 l_2} \left[ \frac{\partial (l_2 u)}{\partial \xi_1} + \frac{\partial (l_1 v)}{\partial \xi_2} + \frac{\partial (l_1 l_2 w)}{\partial N} \right] \bigg|_{N=0} = \frac{1}{l_1 l_2} \left[ \frac{\partial (l_2 u)}{\partial \xi_1} + \frac{\partial (l_1 v)}{\partial \xi_2} + \frac{\partial (l_1 l_2 w)}{\partial N} \right] \bigg|_{N=+\infty}.
\] (5.44)
Since inner velocity \(u\) has to satisfy no-slip boundary condition at \(N = 0\), then at \(N = 0\)
\[
\frac{\partial (l_2 u)}{\partial \xi_1} = 0, \quad \frac{\partial (l_1 v)}{\partial \xi_2} = 0,
\] (5.45)
the definitions of \(l_1, l_2\) can be applied here. Equation (5.44) becomes
\[
\frac{\partial (a_1 a_2 (1 + n\kappa_1)(1 + n\kappa_2) w)}{\partial N} \bigg|_{N=0}
\]
\[
\begin{align*}
\partial(a_2(1+n\kappa_2)u) + \partial(a_1(1+n\kappa_1)v) + \partial(a_1a_2(1+n\kappa_1)(1+n\kappa_2)w) \bigg|_{N=+\infty},
\end{align*}
\]

which gives the leading order equation

\[
\frac{\partial w_0}{\partial N} \bigg|_{N=0} - \frac{\partial w_0}{\partial N} \bigg|_{N=+\infty} = \frac{1}{a_1a_2} \left[ \frac{\partial (a_2u_0)}{\partial \xi_1} + \frac{\partial (a_1v_0)}{\partial \xi_2} \right] \bigg|_{N=+\infty}.
\]

### 5.6 Leading Order Problem for the First Component of Stokes Equation

Now we consider the first component of Stokes equation (5.20), the leading term (dropping tildes for convenience) in \(\nabla^2 (U + u)\) is

\[
\frac{1}{l_2} \frac{\partial}{\partial N} \left[ \frac{l_1}{l_1} \partial(l_1u) \right].
\]

With the definition of \(l_1, l_2\) in (5.34) and generic expansion of \(u\), it can be written as

\[
\frac{1}{a_2(1+n\kappa_2)} \frac{\partial}{\partial N} \left[ \frac{a_2(1+n\kappa_2)}{a_1(1+n\kappa_1)} \frac{\partial (a_1(1+n\kappa_1)u)}{\partial N} \right],
\]

thus, the leading order \(O(\frac{1}{\epsilon^2})\) term coming from \(\nabla^2 (U + u)\) is

\[
\frac{\partial^2 u_0}{\partial N^2},
\]

Similarly, the leading order \(O(\frac{1}{\epsilon^2})\) term coming from \(\nabla P\) is 0, since we have shown \(P_0 = O(1)\), its tangential derivative is also \(O(1)\). And the term coming from \(-\nabla^2 \eta \nabla \phi_o\)

\[
\frac{1}{l_1l_2} \frac{\partial}{\partial N} \left( l_1l_2 \frac{\partial \eta}{\partial N} \right) E_1 = \frac{1}{a_1a_2(1+n\kappa_1)(1+n\kappa_2)} \frac{\partial}{\partial N} \left[ a_1a_2(1+n\kappa_1)(1+n\kappa_2) \frac{\partial \eta}{\partial N} \right] E_1
\]

gives the leading order \(O(\frac{1}{\epsilon^2})\) term

\[
\frac{\partial^2 \eta_0}{\partial N^2} E_{10},
\]

where

\[
E_1 \sim E_{10} + \epsilon E_{11} + ....
\]
Therefore, the leading order equation is
\[
\frac{\partial^2 u_0}{\partial N^2} = \frac{\partial^2 \eta_0}{\partial N^2} E_{10}.
\] (5.54)

We obtain the solution (with \\
\[u_0^+ = (\eta_0^+ - \zeta_+) E_{10^+}, \] (5.55)
where \[\zeta_+ = \eta_+(N = 0)\] is called zeta potential. It is similar to obtain
\[v_0^+ = (\eta_0^+ - \zeta_+) E_{20^+}, \] (5.56)
here we use the fact \[\frac{\partial u_0^+}{\partial N} \to 0\] and \[\frac{\partial v_0^+}{\partial N} \to 0\] when \[N \to +\infty\], which is the result of rescaling \[n = \epsilon N\].

Since we need to compute the \[O(1)\] term of \[\frac{\partial u}{\partial m}\] in later analysis for stress tensors, we have to solve the \[O\left(\frac{1}{\epsilon}\right)\] term from Stokes equation. \[O\left(\frac{1}{\epsilon}\right)\] term coming from \[\nabla P\] is still 0, thus, we shall have the \[O(\epsilon)\] term from
\[
\frac{1}{l_2} \frac{\partial}{\partial N} \left[ \frac{l_2}{l_1} \frac{\partial(l_1 u)}{\partial N} \right] \] (5.57)

to balance the \[O(\epsilon)\] term from
\[
\frac{1}{l_1 l_2} \frac{\partial}{\partial N} \left( l_1 l_2 \frac{\partial \eta}{\partial N} \right) E_1. \] (5.58)

After plugging in the definitions of \[l_1\] and \[l_2\], the balanced equation becomes the \[O(\epsilon)\] term of the following equation
\[
(1 + \epsilon N \kappa_1) \frac{\partial}{\partial N} \left[ \frac{1 + \epsilon N \kappa_2}{1 + \epsilon N \kappa_1} \frac{\partial ((1 + \epsilon N \kappa_1) u)}{\partial N} \right] = - \frac{\partial}{\partial N} \left( (1 + \epsilon N \kappa_1)(1 + \epsilon N \kappa_2) \frac{\partial \eta}{\partial N} \right) E_1, \] (5.59)
where
\[
u = u_0 + \epsilon u_1 + \cdots, \] (5.60)
The $O(\epsilon)$ balanced equation then becomes

$$
\frac{\partial}{\partial N} \left[ \frac{\partial u_1}{\partial N} \right] + \frac{\partial}{\partial N} \left[ N(\kappa_1 + \kappa_2) \frac{\partial u_0}{\partial N} \right] = - \frac{\partial}{\partial N} \left[ \frac{\partial \eta_1}{\partial N} \right] E_{10} - \frac{\partial}{\partial N} \left[ N(\kappa_1 + \kappa_2) \frac{\partial \eta_0}{\partial N} \right] E_{10},
$$

(5.62)

with the leading order solution (5.55), we have the solution

$$
\frac{\partial u_{1+}}{\partial N} = - \frac{\partial \eta_{1+}}{\partial N} E_{10+},
$$

(5.63)

it is similar to obtain

$$
\frac{\partial v_{1+}}{\partial N} = - \frac{\partial \eta_{1+}}{\partial N} E_{20+}.
$$

(5.64)

Now, let’s consider about the Stokes equation (5.18) in ‘−’ region. The same process can be applied to Stokes equation (5.18) to produce the similar solutions for slip velocities with rescaling ratios

$$
u_0 = \frac{\alpha}{\lambda} (\eta_{0-} - \zeta_-) E_{10-},
$$

(5.65)

$$
u_0 = \frac{\alpha}{\lambda} (\eta_{0-} - \zeta_-) E_{20-},
$$

(5.66)

$$
\frac{\partial u_{1-}}{\partial N} = - \frac{\alpha}{\lambda} \frac{\partial \eta_{1-}}{\partial N} E_{10-},
$$

(5.67)

$$
\frac{\partial v_{1-}}{\partial N} = - \frac{\alpha}{\lambda} \frac{\partial \eta_{1-}}{\partial N} E_{10-}.
$$

(5.68)

### 5.7 Stress Tensors

We consider the hydrodynamic stress tensor first with the results above for fluid velocities. The components of the stress tensor $\sigma_{ij}$ can be obtained from the rate of strain ($e_{ij}$), using the relations (dimensionless)

$$
\sigma_{ij+} = -p_+ \delta_{ij} + 2e_{ij+},
$$

(5.69)

$$
\sigma_{ij-} = -p_- \delta_{ij} + 2\lambda e_{ij-}.
$$

(5.70)
Because of the similar analysis for slip velocity field inside the drop, we shall consider the jump of traction across the Debye layer in $'$+$'$ region only, with rescaled dimensionless variables. The components of the rate-of-strain tensor expressed in terms of derivatives of velocity components to the curvilinear system are (dropping tildes)

$$
e_{13} = \frac{1}{2} e_1 \cdot (n \cdot \nabla u) + \frac{1}{2} n \cdot (e_1 \cdot \nabla u) = \frac{\epsilon}{2l_1} \frac{\partial w}{\partial \xi_1} + \frac{1}{2\epsilon} \frac{\partial u}{\partial N}, \quad (5.71)$$

$$
e_{23} = \frac{1}{2} e_2 \cdot (n \cdot \nabla u) + \frac{1}{2} n \cdot (e_2 \cdot \nabla u) = \frac{\epsilon}{2l_2} \frac{\partial w}{\partial \xi_2} + \frac{1}{2\epsilon} \frac{\partial v}{\partial N}, \quad (5.72)$$

$$
e_{33} = n \cdot (n \cdot \nabla u) = \frac{\partial w}{\partial N}. \quad (5.73)$$

Let $T_{H+ij} = \sigma_{ij+} |_{N=0}$ and $T_{Ho+ij} = \sigma_{ij+} |_{N=+\infty}$, using the results that as $N \to +\infty$ the $N-$ derivatives must follow

$$\frac{\partial u}{\partial N} \to 0, \quad \frac{\partial v}{\partial N} \to 0, \quad (5.74)$$

we can obtain the leading order $O(\frac{1}{\epsilon})$ and $O(1)$ jump for tangential components and $O(1)$ jump for normal component

$$T_{H+13} - T_{Ho+13} = \left( \frac{1}{\epsilon} \frac{\partial u_{0+}}{\partial N} + \frac{\partial u_{1+}}{\partial N} \right) \bigg|_{N=0} - \left( \frac{1}{\epsilon} \frac{\partial u_{0+}}{\partial N} + \frac{\partial u_{1+}}{\partial N} \right) \bigg|_{N=+\infty}, \quad (5.75)$$

$$T_{H+23} - T_{Ho+23} = \left( \frac{1}{\epsilon} \frac{\partial v_{0+}}{\partial N} + \frac{\partial v_{1+}}{\partial N} \right) \bigg|_{N=0} - \left( \frac{1}{\epsilon} \frac{\partial v_{0+}}{\partial N} + \frac{\partial v_{1+}}{\partial N} \right) \bigg|_{N=+\infty}, \quad (5.76)$$

$$T_{H+33} - T_{Ho+33} = \left( \frac{\partial w_{0+}}{\partial N} \right) \bigg|_{N=0} - \left( \frac{\partial w_{0+}}{\partial N} \right) \bigg|_{N=+\infty}, \quad (5.77)$$

where we used the equation (5.42) to get the last jump. Similarly,

$$T_{H-13} - T_{Ho-13} = \lambda \left( \frac{1}{\epsilon} \frac{\partial u_{0-}}{\partial N} + \frac{\partial u_{1-}}{\partial N} \right) \bigg|_{N=0} - \left( \frac{1}{\epsilon} \frac{\partial u_{0-}}{\partial N} + \frac{\partial u_{1-}}{\partial N} \right) \bigg|_{N=-\infty}, \quad (5.78)$$

$$T_{H-23} - T_{Ho-23} = \lambda \left( \frac{1}{\epsilon} \frac{\partial v_{0-}}{\partial N} + \frac{\partial v_{1-}}{\partial N} \right) \bigg|_{N=0} - \left( \frac{1}{\epsilon} \frac{\partial v_{0-}}{\partial N} + \frac{\partial v_{1-}}{\partial N} \right) \bigg|_{N=-\infty}, \quad (5.79)$$

$$T_{H-33} - T_{Ho-33} = \left( \frac{\partial w_{0-}}{\partial N} \right) \bigg|_{N=0} - \left( \frac{\partial w_{0-}}{\partial N} \right) \bigg|_{N=-\infty}. \quad (5.77)$$
\[ = \lambda \left( \left. \frac{\partial w_0}{\partial N} \right|_{N=0} - \left. \frac{\partial w_0}{\partial N} \right|_{N=+\infty} \right). \quad (5.80) \]

Electric and osmotic stress tensors are also involved in the stress balance equation, here we express the tensors in Cartesian coordinates and then transform the vectors \( T \cdot n \) into intrinsic coordinates. By the definition of Maxwell and osmotic stress tensors, we have (for '+' region in Cartesian coordinates)

\[
T_{M+} \cdot n = \begin{bmatrix} T_{M+13} \\ T_{M+23} \\ T_{M+33} \end{bmatrix} = \begin{bmatrix} 0 \\ \frac{1}{2} \left( \left( \frac{\partial \phi_+}{\partial x} \right)^2 - \left( \frac{\partial \phi_+}{\partial y} \right)^2 - \left( \frac{\partial \phi_+}{\partial z} \right)^2 \right) \end{bmatrix}, \quad (5.81)
\]

\[
T_{O+} \cdot n = \begin{bmatrix} T_{O+13} \\ T_{O+23} \\ T_{O+33} \end{bmatrix} = - \begin{bmatrix} 0 \\ \frac{1}{2} \left( \left( \frac{\partial \eta_+}{\partial x} \right)^2 - \left( \frac{\partial \eta_+}{\partial y} \right)^2 - \left( \frac{\partial \eta_+}{\partial z} \right)^2 \right) \end{bmatrix}, \quad (5.82)
\]

the leading order transformation into intrinsic coordinates is

\[
T_{M+} \cdot n = \begin{bmatrix} T_{M+13} \\ T_{M+23} \\ T_{M+33} \end{bmatrix} = \begin{bmatrix} 0 \\ \frac{1}{2} \left( \left( \frac{\partial \phi_+}{\partial \xi_1} \right)^2 - \left( \frac{\partial \phi_+}{\partial \xi_2} \right)^2 - \left( \frac{\partial \phi_+}{\partial \xi_3} \right)^2 \right) \end{bmatrix}, \quad (5.83)
\]

\[
T_{O+} \cdot n = \begin{bmatrix} T_{O+13} \\ T_{O+23} \\ T_{O+33} \end{bmatrix} = - \begin{bmatrix} 0 \\ \frac{1}{2} \left( \left( \frac{\partial \eta_+}{\partial \xi_1} \right)^2 - \left( \frac{\partial \eta_+}{\partial \xi_2} \right)^2 - \left( \frac{\partial \eta_+}{\partial \xi_3} \right)^2 \right) \end{bmatrix}. \quad (5.84)
\]

In quasi-steady state of charging process, we know that

\[
\frac{\partial (\phi_+ - \eta_+)}{\partial n} = \frac{\phi_{0+}}{\partial n} = 0, \quad (5.85)
\]
thus, we have

\[ T_{M+} \cdot n + T_{O+} \cdot n = \left[ \frac{1}{l_1} \frac{\partial \phi_+}{\partial \xi_1} \cdot \frac{\partial \eta_+}{\partial n} + \frac{1}{l_2} \frac{\partial \phi_+}{\partial \xi_2} \cdot \frac{\partial \eta_+}{\partial n} \right] \] (5.86)

In ‘−’ region, \( T_{M−} \cdot n \) and \( T_{O−} \cdot n \) need to be discussed too. We can have the similar formula for \( T_{M−} \cdot n + T_{O−} \cdot n \):

\[ T_{M−} \cdot n + T_{O−} \cdot n = \left[ \frac{1}{l_1} \frac{\partial \phi_−}{\partial \xi_1} \cdot \frac{\partial \eta_−}{\partial n} + \frac{1}{l_2} \frac{\partial \phi_−}{\partial \xi_2} \cdot \frac{\partial \eta_−}{\partial n} \right] \] (5.87)

Now the stress balance equation (5.13) becomes

\[ \left[ T_H \cdot n \right]^- = \frac{2\kappa n}{Ca} \left[ \frac{1}{l_1} \frac{\partial \phi_+}{\partial \xi_1} \cdot \frac{\partial \eta_+}{\partial n} + \frac{1}{l_2} \frac{\partial \phi_+}{\partial \xi_2} \cdot \frac{\partial \eta_+}{\partial n} \right] + \alpha \left[ \frac{1}{l_1} \frac{\partial \phi_−}{\partial \xi_1} \cdot \frac{\partial \eta_−}{\partial n} + \frac{1}{l_2} \frac{\partial \phi_−}{\partial \xi_2} \cdot \frac{\partial \eta_−}{\partial n} \right] \] (5.88)

which is the stress jump across the interface when \( N = 0 \). Now, we apply (5.75), (5.76), (5.77) and (5.88) into (5.1) to get final jump in traction which is used in BIE:

\[ \left[ T_{Ho} \cdot n \right]^- = \left[ T_H \cdot n \right]^- + (T_{Ho+} \cdot n - T_{Ho−} \cdot n) - (T_{Ho−} \cdot n - T_{Ho+} \cdot n) \]

\[ = \frac{2\kappa n}{Ca} \left[ \frac{1}{l_1} \frac{\partial \phi_+}{\partial \xi_1} \cdot \frac{\partial \eta_+}{\partial n} + \frac{1}{l_2} \frac{\partial \phi_+}{\partial \xi_2} \cdot \frac{\partial \eta_+}{\partial n} \right] \]
\[
+ \alpha \left[ \begin{array}{c}
\frac{1}{t_1} \frac{1}{\nu_{21}} \left( \frac{\partial \phi_{\nu_1}}{\partial \xi_1} \right)^2 - \left( \frac{\partial \phi_{\nu_1}}{\partial \xi_2} \right)^2 \right] + \frac{1}{t_2} \left( \frac{\partial \eta_{\nu_1}}{\partial \xi_1} \right)^2 - \left( \frac{\partial \eta_{\nu_1}}{\partial \xi_2} \right)^2 \right] + \lambda \left[ \begin{array}{c}
\left( \frac{1}{\epsilon} \frac{\partial u_{\nu_1}}{\partial N} + \frac{\partial u_{1+}}{\partial N} \right) \bigg|_{N=0} \\
\left( \frac{1}{\epsilon} \frac{\partial v_{\nu_1}}{\partial N} + \frac{\partial v_{1+}}{\partial N} \right) \bigg|_{N=0} \\
\frac{\partial w_{\nu_1}}{\partial N} \bigg|_{N=0} - \frac{\partial w_{0+}}{\partial N} \bigg|_{N=+\infty} \\
\left( \frac{1}{\epsilon} \frac{\partial u_{\nu_1}}{\partial N} + \frac{\partial u_{1-}}{\partial N} \right) \bigg|_{N=0} \\
\left( \frac{1}{\epsilon} \frac{\partial v_{\nu_1}}{\partial N} + \frac{\partial v_{1-}}{\partial N} \right) \bigg|_{N=0} \\
\frac{\partial w_{\nu_1}}{\partial N} \bigg|_{N=0} - \frac{\partial w_{0-}}{\partial N} \bigg|_{N=+\infty}
\end{array} \right] + \ldots \right]
\]

\[
O\left(\frac{1}{\epsilon}\right) \text{ and } O(1) \text{ terms of the first and second components of the second and third terms on the right hand side cancel out with the expression of } u_{0\pm} , u_{1\pm} , v_{0\pm} \text{ and } v_{1\pm} \text{ in (5.55, 5.56, 5.63, 5.64, 5.65 - 5.68).}
\]

\section{5.8 Quasi-Steady State Electro-kinetic Flow}

Based on the assumption for time scales \( T_C \ll T_F \), we assume the quasi-steady state of charging process for both exterior and interior. The constant potential solution in outer field of ’-’ region with Neumann boundary condition is

\[
\phi_{o-} \equiv 0,
\]

(5.90)
thus, the drop doesn’t support any electric field in the outer field of ’−’ region. Recall (5.18), there is no body force for the Stokes equation inside the drop. By analogy, we find the following solutions

\[ \mathbf{v} \equiv 0, \quad \eta \big|_{N=0} \equiv \phi \big|_{N=0}, \]  

(5.91)

therefore, the effects given by the slip velocity and stress in ’−’ region can be vanished in quasi-steady state electro-kinetic flow. The ’+’ region will be required to analyze only.

For axisymmetric model, \( \frac{\partial}{\partial \xi_2} = 0 \) and \( a_1 = \left| \frac{\partial \mathbf{X}}{\partial \xi_2} \right| = 1 \), we only need to calculate

\[ \frac{\partial \eta_+}{\partial \xi_1} \bigg|_{N=0}^N \quad \text{and} \quad \left( \frac{\partial \eta_+}{\partial N} \bigg|_{N=0}^N - \frac{\partial \eta_+}{\partial N} \bigg|_{N=+\infty} \right). \]

From (5.47) we have

\[ \frac{\partial w_{0+}}{\partial N} \bigg|_{N=0}^N - \frac{\partial w_{0+}}{\partial N} \bigg|_{N=+\infty} = \frac{1}{a_1 a_2} \left[ \frac{\partial (a_2 u_{0+})}{\partial \xi_1} + \frac{\partial (a_1 v_{0+})}{\partial \xi_2} \right] \bigg|_{N=+\infty}. \]  

(5.92)

In that case, the terms with \( \frac{\partial w_{0+}}{\partial N} \) can be computed numerically by first computing slip velocities \( u_{0+} \) and \( v_{0+} \). They are in fact related with the second tangential derivative of the electric potential in the outer and inner Laplace equations.

In order to compute \( \frac{\partial \eta_+}{\partial \xi_1} \bigg|_{N=0}^N \), we can use the equation

\[ \frac{\partial \eta_+}{\partial \xi_1} \bigg|_{N=0}^N = \frac{\partial (\phi_s - \phi_{o+})}{\partial \xi_1}, \]  

(5.93)

where \( \phi_s \) means the total potential on the interface \( N = 0 \), which is given by the exact solution of Poisson-Boltzmann equation:

\[ \phi_s = \frac{1}{\Psi} \ln \frac{\alpha^2 - 1 - \alpha \left( e^{\Psi (\phi_{o-} - \phi_{o+})} - e^{\Psi (\phi_{o+} - \phi_{o-})} \right)}{\alpha^2 e^{-\Psi \phi_{o-}} - e^{-\Psi \phi_{o+}}}, \]  

(5.94)

with \( \phi_{o-} \equiv 0 \), thus,

\[ \phi_s = \frac{1}{\Psi} \ln \frac{\alpha + e^{\Psi \phi_{o+}}}{\alpha + e^{-\Psi \phi_{o+}}}. \]  

(5.95)
Finally, \( \frac{\partial \phi_{o+}}{\partial \xi_1} \bigg|_{n=0} \) can be solved numerically by the outer solution of Laplace equation \( \nabla^2 \phi = 0 \). For axi-symmetric case, let \( s- \) direction be the tangential direction. Applying the solution for \( u_0 \),

\[
\frac{\partial u_0}{\partial s} = \frac{\partial}{\partial s} \left[ (\phi_s - \phi_{o+}) \frac{\partial \phi_{o+}}{\partial s} \right] \\
= \frac{\partial}{\partial s} (\phi_s - \phi_{o+}) \frac{\partial \phi_{o+}}{\partial s} + (\phi_s - \phi_{o+}) \frac{\partial^2 \phi_{o+}}{\partial s^2} \tag{5.96}
\]

By the definition of \( \phi_s \), we have

\[
\frac{\partial \phi_s}{\partial s} = \frac{1}{2} \frac{\partial \phi_{o+}}{\partial s} \left( \frac{e^{\frac{\Psi}{2} \phi_{o+}}}{\alpha + e^{\frac{\Psi}{2} \phi_{o+}}} + \frac{1}{\alpha e^{\frac{\Psi}{2} \phi_{o+}} + 1} \right). \tag{5.97}
\]

Thus,

\[
\frac{\partial u_0}{\partial s} = \left[ \frac{1}{2} \left( \frac{e^{\frac{\Psi}{2} \phi_{o+}}}{\alpha + e^{\frac{\Psi}{2} \phi_{o+}}} + \frac{1}{\alpha e^{\frac{\Psi}{2} \phi_{o+}} + 1} \right) - 1 \right] \left( \frac{\partial \phi_{o+}}{\partial s} \right)^2 + (\phi_s - \phi_{o+}) \frac{\partial^2 \phi_{o+}}{\partial s^2}, \tag{5.98}
\]

when \( \alpha = 1 \), it can be simplified as

\[
\frac{\partial u_0}{\partial s} = -\frac{1}{2} \left( \frac{\partial \phi_{o+}}{\partial s} \right)^2 + \frac{1}{2} \phi_{o+} \frac{\partial^2 \phi_{o+}}{\partial s^2}. \tag{5.99}
\]
CHAPTER 6
SMALL DEFORMATION ANALYSIS

In this chapter, we summarize the small deformation theory for the drop. The small perturbation analysis has been widely used to study the dynamics of a droplet and lipid bilayer vesicle for both hydrodynamics and electrohydrodynamics, see [26, 27, 28, 29, 30]. We study the effect of electro-osmosis and slip velocity on the drop deformation for small perturbations. The leading order asymptotic theory is developed and briefly discussed next. The analytical results can be used as a check on the numerical calculations.

6.1 Drop Shape

We follow the general small deformation theory for a nearly spherical drop. For our axi-symmetric model, in a spherical coordinate system centered at the drop, the position of the interface is

\[ r_s(\theta, t) = 1 + f(\theta, t), \]  

(6.1)

where \( f \) measures the deviation from sphericity and is expanded in spherical harmonics \( Y_j \) (in axi-symmetric model):

\[ f(\theta, t) = \sum_{j \geq 2} f_j(t)Y_j(\theta), \]  

(6.2)

\[ Y_j = \frac{(2j + 1)}{4\pi} P_j(\cos \theta), \]  

(6.3)

we follow [30]’s conclusion that the \( j = 1 \) modes have been omitted because they are for the translation of the center of mass. \( P_j(\cos \theta) \) are the Legendre polynomials, for example:

\[ P_1(\cos \theta) = \cos \theta, \]  

(6.4)
\[ P_2(\cos \theta) = \frac{1}{2}(3 \cos^2 \theta - 1), \quad (6.5) \]
\[ P_3(\cos \theta) = \frac{1}{2}(5 \cos^3 \theta - 3 \cos \theta). \quad (6.6) \]

The vector spherical harmonics are defined as

\[ y_{j0} = [j(j + 1)]^{-\frac{1}{2}} r \frac{\partial Y_j}{\partial \theta} \cdot \mathbf{t}, \quad (6.7) \]
\[ y_{j2} = \mathbf{r} Y_j, \quad (6.8) \]

where \( \mathbf{t} \) is the unit tangential vector, \( \mathbf{r} = \mathbf{r}/r \), \( y_{j0} \) is tangential and \( y_{j2} \) is normal to a sphere in axisymmetric case. For example:

\[ y_{20} = -\frac{3}{2} \sqrt{\frac{5}{6\pi}} \cdot r \sin \theta \cdot \cos \theta \cdot \mathbf{t}, \quad (6.9) \]
\[ y_{22} = \frac{1}{4r} \sqrt{\frac{5}{\pi}} (3 \cos^2 \theta - 1) \cdot \mathbf{r}. \quad (6.10) \]

### 6.2 Evolution Equation

We let \( \mathbf{u}_s \) denote the velocity of the interface. The evolution of the interface is governed by the kinematic equation:

\[ \frac{\partial F}{\partial t} + \mathbf{u}_s \cdot \nabla F = 0, \quad (6.11) \]

The function \( F(\mathbf{r}, t) \) represents the interface shape as the set of points \( \mathbf{r} \), where \( F(\mathbf{r}, t) \equiv 0 \), and it is given by

\[ F(\mathbf{r}, t) = r - r_s(\theta, t), \quad (6.12) \]

where \( r_s \) is defined in previous section.

### 6.3 Multipole Representation of Fluid Velocities

In this section, we develop the multipole expansion for outer fluid velocities in '+-' and '-+' regions in order to apply them into the kinematic equation (6.11). The
classical Lamb’s solution tells us the velocity field and pressure field in all space if the velocity field is specified on a sphere with radius \( r \). We adjust the 3-D model into 3-D axi-symmetric model, thus, Lamb’s solution uses the two vectors as we defined in the previous section.

The outer velocities in \('+\) and \('−\) regions are defined as:

\[
\begin{align*}
\mathbf{v}_+(r) &= \sum_{jq} c_{jq}^+ u_{jq}^+(r) = \sum_{j} (c_{j0}^+ u_{j0}(r) + c_{j2}^+ u_{j2}(r)), \\
\mathbf{v}_-(r) &= \sum_{jq} c_{jq}^- u_{jq}^-(r) = \sum_{j} (c_{j0}^- u_{j0}(r) + c_{j2}^- u_{j2}(r)),
\end{align*}
\]

(6.13)

(6.14)

on the sphere \( r = 1 \), these velocity fields reduce to

\[
\mathbf{u}_{jq}^\pm = y_{jq}, \quad q = 0, 2.
\]

(6.15)

Since there is the no slip velocity in \('−\) region, as \( r \to 1 \), \( \mathbf{u}_s = \mathbf{v}_- \). Similarly as [30]’s analysis, the deviation of the interface is determined from the kinematic equation (6.11)

\[
\frac{\partial f_j}{\partial t} = c_{j2}^-, \quad r = 1.
\]

(6.16)

Since there is a slip velocity in \('+\) region, we have

\[
\mathbf{v}_+ = \mathbf{v}_- + \mathbf{v}_{slip}, \quad r = 1,
\]

(6.17)

where \( \mathbf{v}_{slip} \) is the slip velocity which is the inner region velocity for \( N \to +\infty \), as we solved before.

For simplicity, we discuss the case \( \alpha = K = 1 \) at first for the small deformation theory. In this case, the slip velocity can be easily written into terms of harmonic vectors. We will also consider the case for any \( \alpha \) but \( \Psi \ll 1 \) which is the regular limit for small dimensionless surface potential (small applied E-field), this assumption is reasonable for small deformation theory with small capillary number. In that case, we need to expand slip velocity and try to obtain the leading order term.
Case 1) \( \alpha = 1 \): For a sphere with radius \( r = 1 \), the slip velocity can be written into the form
\[
v_{\text{slip}} = \frac{9}{16} \sin(2\theta) t,
\]  
where \( t \) denotes the tangential direction. By the definition for vectors in spherical harmonic, we have
\[
v_{\text{slip}} = -\frac{3}{4} \sqrt{\frac{6\pi}{5}} y_{20}.
\]  

Then the equation (6.17) gives the relation of coefficients
\[
c_{20}^+ = c_{20}^- - \frac{3}{4} \sqrt{\frac{6\pi}{5}},
\]
\[
c_{j0}^+ = c_{j0}^-, \quad j > 2,
\]
\[
c_{j2}^+ = c_{j2}^-; \quad j \geq 2.
\]

6.4 Stress Balance Equation

In this section, we discuss the normal stress balance equation which includes the curvature variations for small deformation of the shape. The leading order solution \( f_2 \) will be determined by applying the previous expansion.

Recall the stress balance equation (5.89), as \( \alpha = K = 1 \) for axi-symmetric model, we have
\[
\eta_+|_{N=0} = \phi_s - \phi_{o+} = -\frac{1}{2} \phi_{o+},
\]
\[
\phi_+|_{N=0} = \frac{1}{2} \phi_{o+}.
\]

It is also convenient to write all quantities into the terms defined for small deformation theory, when \( r = 1 \)
\[
\frac{\partial w}{\partial N}|_{N=0} - \frac{\partial w}{\partial N}|_{N=+\infty} = \frac{\partial v_{\text{slip}}}{\partial s} = \frac{9}{8} \cos(2\theta) = 3 \sqrt{\frac{\pi}{5}} Y_2 - \frac{3}{8}.
\]
The curvature for small perturbation is

\[ \kappa = 1 + \frac{1}{2}(j + 2)(j - 1)f_j Y_j, \ j \geq 2. \]  \hspace{1cm} (6.26)

The constant parts in right hand side of (5.89) are balanced by the pressure jump, therefore, the stress balance equations for two components (tangential and normal) are obtained as follows

\[ (\tau^+_j - \lambda \tau^-_j) \cdot y_{j0} = 0, \]  \hspace{1cm} (6.27)

\[ (\tau^+_j - \lambda \tau^-_j) \cdot y_{j2} = \left[ \frac{1}{Ca}(j + 2)(j - 1)f_j Y_j - 3\sqrt{\frac{\pi}{5}}Y_2 \right] \cdot n, \]  \hspace{1cm} (6.28)

where \( \lambda \) is the ratio of viscosities, the hydrodynamic tractions associated with the velocity fields in both \( '+' \) and \( '-' \) regions are defined as

\[ \tau^-_{j0} = (2j + 1)c^-_{j0} - 3 \left( \frac{j + 1}{j} \right)^\frac{1}{2} c^+_{j2}, \]  \hspace{1cm} (6.29)

\[ \tau^+_{j0} = -(2j + 1)c^+_{j0} + 3 \left( \frac{j}{j + 1} \right)^\frac{1}{2} c^-_{j2}, \]  \hspace{1cm} (6.30)

\[ \tau^-_{j2} = -3 \left( \frac{j + 1}{j} \right)^\frac{1}{2} c^-_{j0} + \frac{3 + j + 2j^2}{j} c^-_{j2}, \]  \hspace{1cm} (6.31)

\[ \tau^+_{j2} = 3 \left( \frac{j}{j + 1} \right)^\frac{1}{2} c^+_{j0} - \frac{4 + 3j + 2j^2}{j + 1} c^+_{j2}, \]  \hspace{1cm} (6.32)

we then apply these tractions into equations (6.27) and (6.28) with utilizing the relation of \( c^\pm_{jq} \) in (6.20), (6.21) and (6.22). Finally the leading order solution for \( f_2 \) is

\[ c^+_{22} = -\frac{40(\lambda + 1)}{(38\lambda^2 + 89\lambda + 48)Ca} f_2 + \frac{15(7\lambda + 4)}{76\lambda^2 + 178\lambda + 96} \sqrt{\frac{\pi}{5}}, \]  \hspace{1cm} (6.33)

which can be plugged into kinematic equation (6.16) in order to get the time dependent ODE for \( f_2 \)

\[ \frac{\partial f_2}{\partial t} + \frac{40(\lambda + 1)}{(38\lambda^2 + 89\lambda + 48)Ca} f_2 = \frac{15(7\lambda + 4)}{76\lambda^2 + 178\lambda + 96} \sqrt{\frac{\pi}{5}}. \]  \hspace{1cm} (6.34)
With initial spherical shape, the solution is

\[
f_2(t) =\frac{3(7\lambda + 4)}{16(\lambda + 1)} \sqrt{\frac{\pi}{5}} Ca \left(1 - e^{-\frac{40(\lambda + 1)}{138(\lambda + 8\lambda + 48)Ca^4}} t\right), \tag{6.35}
\]

when \(\lambda = 1\), it is

\[
f_2(t) =\frac{33}{32} \sqrt{\frac{\pi}{5}} Ca \left(1 - e^{-\frac{16\Psi}{32\Psi^2 \pi} t}\right). \tag{6.36}
\]

### 6.5 Asymptotic Drop Deformation Degree

The degree of drop deformation is characterized using the classical deformation parameter \(D = (a - b)/(a + b)\), where \(a\) and \(b\) represent the half-length (parallel to the electric direction) and half-breadth (perpendicular to the electric direction) of the drop, respectively. For steady state \(t \to \infty\), the leading order parameters are

\[
r \approx 1 + f_2 Y_2 = 1 + \frac{3(7\lambda + 4)Ca}{64(\lambda + 1)} \left(3 \cos^2 \theta - 1\right), \tag{6.37}
\]

\[
a = 1 + \frac{3(7\lambda + 4)Ca}{32(\lambda + 1)}, \quad \theta = 0, \tag{6.38}
\]

\[
b = 1 - \frac{3(7\lambda + 4)Ca}{64(\lambda + 1)}, \quad \theta = \pi/2, \tag{6.39}
\]

\[
D = \frac{9(7\lambda + 4)Ca}{128(\lambda + 1) + 3(7\lambda + 4)Ca}. \tag{6.40}
\]

(Case 2) any \(\alpha\) and \(\Psi \ll 1\): In this case, it is necessary to expand the slip velocity which is (for a sphere \(r = 1\))

\[
v_{\text{slip}} = -\zeta E_t = -(\phi_s - \phi_o) E_t
\]

\[
= -\left(\frac{1}{\Psi} \ln \frac{\alpha + e^{\frac{3\Psi}{4} \cos \theta}}{\alpha + e^{-\frac{3\Psi}{4} \cos \theta}} - \frac{3}{2} \cos \theta\right) \cdot \left(\frac{3}{2} \sin \theta\right) t. \tag{6.41}
\]

Asymptotic expansion gives

\[
\ln \frac{\alpha + e^{\frac{3\Psi}{4} \cos \theta}}{\alpha + e^{-\frac{3\Psi}{4} \cos \theta}} = \frac{3\Psi}{2(\alpha + 1)} \cos \theta - \frac{9(2 - \alpha)}{64(\alpha + 1)^2} \Psi^2 \cos^3 \theta + O(\Psi^4). \tag{6.42}
\]
The leading order terms of the potentials are
\[ \phi_+|_{N=0} = \phi_s \approx \frac{3}{2(\alpha + 1)} \cos \theta, \] (6.43)
\[ \eta_+|_{N=0} = \phi_s - \phi_o+ \approx -\frac{3\alpha}{2(\alpha + 1)} \cos \theta. \] (6.44)

Their tangential derivatives are obtained
\[ \frac{\partial \phi_+}{\partial s}|_{N=0} \approx -\frac{3}{2(\alpha + 1)} \sin \theta, \] (6.45)
\[ \frac{\partial \eta_+}{\partial s}|_{N=0} \approx \frac{3\alpha}{2(\alpha + 1)} \sin \theta, \] (6.46)

which give the term in the stress balance equation (5.89)
\[ \frac{1}{2} \left[ \left( \frac{\partial \eta_+}{\partial s} \right|_{N=0} \right)^2 - \left( \frac{\partial \phi_+}{\partial s} \right|_{N=0} \right)^2 \approx \frac{9(\alpha - 1)}{8(\alpha + 1)} \sin^2 \theta \]
\[ = -\frac{3(\alpha - 1)}{2(\alpha + 1)} \sqrt{\pi} \frac{Y_2}{5} + \frac{3(\alpha - 1)}{4(\alpha + 1)}. \] (6.47)

The leading order term of slip velocity is
\[ \mathbf{v}_{\text{slip}} \approx \frac{9\alpha}{8(\alpha + 1)} \sin(2\theta) \cdot \mathbf{t}, \] (6.48)

which gives
\[ \frac{\partial w}{\partial N}|_{N=0} - \frac{\partial w}{\partial N}|_{N=+\infty} = \frac{\partial v_{\text{slip}}}{\partial s} = \frac{6\alpha}{(\alpha + 1)} \sqrt{\frac{\pi}{5}} Y_2 - \frac{3\alpha}{4(\alpha + 1)}. \] (6.49)

The normal component of stress balance equation (6.28) then is
\[ (\tau_j^+ - \lambda \bar{\tau}_j) \cdot \mathbf{y}_j = \left[ \frac{1}{Ca} (j + 2)(j - 1) f_j Y_j - \frac{3(3\alpha + 1)}{2(\alpha + 1)} \sqrt{\frac{\pi}{5}} Y_2 \right] \cdot \mathbf{n}. \] (6.50)

After the same calculation process as previous, we obtain the similar solutions for \( f_2 \) and \( D \):
\[ f_2(t) = \frac{3(\lambda + 1) + 9(2\lambda + 1)\alpha}{8(\lambda + 1)(\alpha + 1)} \sqrt{\frac{\pi}{5}} Ca \left( 1 - e^{-\frac{40(\lambda+1)}{(8\lambda^2 + 29\lambda + 18)Ca} t} \right), \] (6.51)
\[ D = \frac{a - b}{a + b} = \frac{[9(\lambda + 1) + 27(2\lambda + 1)\alpha]Ca}{64(\lambda + 1)(1 + \alpha) + [3(\lambda + 1) + 9(2\lambda + 1)\alpha]Ca}. \] (6.52)
CHAPTER 7
NUMERICAL IMPLEMENTATION

7.1 Outer Laplace Equation

The numerical method is constructed in the spirit of matched asymptotic analysis. We use asymptotics to derive a solution for the electric field flow and ion densities in the Debye layer. We also solve the leading order flow equations in the layer. Indeed, we have already presented the solution for the electric field and ion densities in the layer (cf. equations (2.91)-(2.98)). We are currently deriving the solution to the flow equations. These solutions will contain undetermined functions which are fixed by matching to the outer far-field flow. In the analysis of Chapter 2 for a spherical drop, the outer flow is known analytically, and the matching coefficients could be easily determined. For a drop of arbitrary (non-spherical) shape, the outer solution will be determined using the boundary integral method.

As an example, we consider the problem for the electric field and ion concentration in the case when the charging time scale is much less than the time scale for fluid motion, i.e., \( T_C \ll T_F \). In this case, we want the quasi-steady state solution for the electrostatic field which satisfies \( \nabla \phi \cdot n = 0 \) on the surface of the drop (cf. Figure 2.1). Therefore, we need to solve Laplace’s equation in infinite domain outside the drop with Neumann boundary conditions on a surface of the arbitrary shape. We solve this problem using the boundary-integral method by first decomposing the potential into a far-field component \( \phi^\infty \) and a disturbance component \( \phi^D \) due to the body [31]:

\[
\phi = \phi^\infty + \phi^D. \tag{7.1}
\]
The comparison of numerical and analytical solutions for the outer potential problem in ‘+’ region. We use boundary integral method to solve the Laplace equation with Neumann boundary condition. We assume the dimensionless far-field electric field $E_\infty = 1$. The problem for the spherical drop with radius $r = 1$ is axi-symmetric, so that the potential of the point on the surface is only dependent on its $x$ position ($x$ direction is the same as the electric field).

The boundary-integral representation for $\phi_D$ is:

$$\phi^D = - \int_S G(x, x_0)[n(x) \cdot \nabla \phi^D(x)]dS(x) + \int_S \phi^D(x)[n(x) \cdot \nabla G(x, x_0)]dS(x). \quad (7.2)$$

This is a second kind integral equation. The equation is well conditioned, and is solved by iteration.

As a check, we have solved (7.2) in the simple case of a spherical drop. Figure 7.1 gives a comparison of the known analytical solution and the numerically computed solution, with good agreement.


### 7.2 High Order Quadratures for Laplace Equation

From the asymptotic analysis for inner problems, we have obtained the boundary integral representation for interfacial velocity which is related with the solution of outer Laplace equation and its first and second tangential derivatives. It is given in (4.25) and (5.99).

The Laplace equation \( \nabla^2 \phi = 0 \) can be solved approximately by some numerical methods, e.g., boundary elements. The tangential derivatives of the solution \( \phi_{num} \) will converge at a reduced rate of accuracy, especially when the relative error of \( \phi_{num} \) is very small. The reduction of the rate of accuracy is proportional to the order of derivatives. Therefore, in order to compute the interfacial velocity with a fixed order of accuracy, e.g., two in our implementation, we have to either compute numerical approximations of tangential derivatives \( \partial^n \phi / \partial s^n \) of \( \phi \) with the same accuracy as numerical solution \( \phi_{num} \) or compute \( \phi_{num} \) with higher order of accuracy and then take the derivatives by direct methods, e.g., finite difference or FFT.

The first approach was studied in [32, 33], they derived a hierarchy of boundary integral equations for \( \partial^n \phi / \partial s^n \) by differentiating the boundary integral equation for \( \phi \) and solved the new boundary integral equations numerically with the same accuracy as the initial Laplace equation. However, we have not developed those formulae and save it for our future work.

We instead solved the Laplace equation with 4th order of accuracy to make sure the 2nd order of accuracy for \( \partial^2 \phi_{num} / \partial s^2 \). Boundary element methods are implemented in our numerical simulation. More precisely, the high order isoparametric cubic-splines are used for our boundary element discretization to approximate \( \phi \) and \( \partial \phi / \partial n \) over the \( i \)th element \( (s_i < s < s_{i+1}) \)

\[
\phi \approx \sum_{j=1}^{N+1} \left[ A_{ij} (s - s_i)^3 + B_{ij} (s - s_i)^2 + C_{ij} (s - s_i) + \delta_{ij} \right] \phi_j, \quad (7.3)
\]

\[
\frac{\partial \phi}{\partial n} \approx \sum_{j=1}^{N+1} \left[ A_{ij} (s - s_i)^3 + B_{ij} (s - s_i)^2 + C_{ij} (s - s_i) + \delta_{ij} \right] \frac{\partial \phi_j}{\partial n}, \quad (7.4)
\]
where $N+1$ is total number of nodes, coefficient matrices $A$, $B$ and $C$ are calculated by the continuities of $\phi$ and its derivatives on each node. The linear system with a tridiagonal matrix need to solved, which is listed in Appendix A. The first formula can also be used for computing the first and second order tangential derivatives $\partial \phi / \partial s$ and $\partial^2 \phi / \partial s^2$ after obtaining $\phi$.

The integrands on regular elements are computed accurately by the \textit{Gauss-Legendre quadrature} while the integrands on singular elements are computed by \textit{Hybrid Gauss-Trapezoidal quadrature} in [34] because of the logarithmic performance of the singularities. Some of the details are as follows.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{axisymmetric_model.png}
\caption{Geometry of axisymmetric model.}
\end{figure}
Given an axi-symmetric surface $S$ as Figure 7.2 shows, with trace $C$ which is parametrized by

$$C : \mathbf{x} = (x(s), y(s)),$$

(7.5)

where $s$ is the arclength, we have the corresponding integral equation for Laplace equation

$$\begin{align*}
\phi(x_0, y_0) &= -2 \int_C G_{AX}(x, y, x_0, y_0) \left[ \mathbf{n}(x) \cdot \nabla \phi(x) \right] y(x) \, dl(x) \\
& \quad + 2 \int_C P.V. \phi(x) \left[ \mathbf{n}(x) \cdot \nabla G_{AX}(x, y, x_0, y_0) y(x) \right] dl(x).
\end{align*}$$

(7.6)

**Figure 7.3** Accuracy for solutions of Laplace equation.

$G_{AX}(x, y, x_0, y_0)$ is the free-space axisymmetric Green’s function, which is shown in Appendix B.
We also show in Appendix B that both $G_{AX}(x, y, x_0, y_0)$ and its normal
derivative $\partial G_{AX}(x, y, x_0, y_0)/\partial n$ have singular behaviors as $x \to x_0$ and $y \to y_0$ when
$y_0 \neq 0$. Thus, the Hybrid Gauss-Trapezoidal quadrature method becomes important
when evaluating the singular integrands for single and double potentials. Figure 7.3
shows the order of accuracy for $\phi_{num}$, $\partial \phi_{num}/\partial s$ and $\partial^2 \phi_{num}/\partial s^2$.

7.3 Boundary Integral Method for Stokes Equation

The electric potential field is required for the computation of the slip velocity and
fluid velocity field. For a given interfacial velocity, $\phi_{num}$, $\partial \phi_{num}/\partial s$ and $\partial^2 \phi_{num}/\partial s^2$
are computed independently of the flow with required accuracy, we can obtain the slip
velocity and the force jump for solving our modified boundary integral equation (4.25).
The same cubic splines discretization method is used here and linear collocation
method is applied in order to compute the velocity field with required second order
accuracy. For solving the single and double layer potential in boundary integral
representation for Stokes equation, we found it convenient to use Gauss-Legendre
quadrature for regular integrals and remove the weak singularities or use Hybrid
Gauss-Trapezoidal quadrature for singular integrals, we have used some routines from
[35] here. The procedure for advancing the interface is then briefly described next.

We consider an initially spherical drop at rest when a uniform electric field
is applied at $t = 0$. The system is characterized by the property ratios $K$
(conductivities), $\alpha$ (permittivities), $\lambda$ (viscosities), dimensionless surface potential
$\Psi$ and dimensionless electric capillary number $Ca$. The effect caused by the physical
property ratio $\alpha$ (permittivities) only comes from the boundary condition. The reason
of that is we assume the faster time scale for charging, it gives us the 0-slip velocity
in inner region as we have shown in the analysis for Stokes equations, which means
the slip velocity in $'-$ region is independent of $\alpha$. In order to check our numerical
method, we consider the weak electric fields first. In that case, the capillary number
$Ca$ is small, we then follow the drop deformation in time by integrating the kinematic condition

$$\frac{\partial x}{\partial t} = u_n(x)n(x),$$  \hspace{1cm} (7.7)

where $x$ is a marker point on the interface and $u_n$ is the normal component of the interfacial velocity.

The problem we want to solve numerically consists of the discretized versions of Laplace equation for outer region electric potential, the boundary integral equation for interfacial velocity and the kinematic equation for interfacial marker point. We follow the classical and straightforward scheme to solve these highly coupled equations.

Step 1: For a given shape at time $t$, we solve the Laplace equation numerically and then calculate the interfacial velocity from the boundary integral equation.

Step 2: The shape of the interface is updated for time $t + \delta t$ by integrating the kinematic equation.

Step 3: The new shape in Step 2 is used in Step 1 recursively.
CHAPTER 8

NUMERICAL RESULTS

The numerical study is based on the assumption that charging process is at quasi-steady state for any shape of the drop. The case with equal viscosities will be discussed first while the viscosity effect will be studied later. Both numerical and analytical results show that the drop deforms into a prolate shape: $D > 0$, which means the drop will elongate in the direction of the applied electric field till it arrives at the steady state or breaks up. During our numerical experiment, the half interface profile of the axi-symmetric problem is divided into $N$ equal elements defining $N + 1$ nodes, with the two extreme nodes lying on the axis. $N = 160$ in the following results, time step is chosen approximately $10^{-4}$. The numerical steady state is obtained when the maximum dimensionless normal velocity is less than the tolerance which is very small (typically $10^{-4}$).

8.1 Small Deformation and Breakup

We simulate the case with equal viscosities and $\alpha = K$ for simplicity first. For the given set of parameters $(\lambda, \Psi) = (1, 0.01)$ and any $\alpha > 0$, the leading order asymptotic solution matches the numerical solution very well when $D < 0.05$, see Figure 8.1. Above this value, the difference between the solid and diamond lines increase and high order small deformation theory is required to achieve the prediction, however, we save that for our further work. Smaller deformation for smaller $\alpha$ and better agreement for the case $\alpha = 1$ is shown in our numerical simulation, this is also well explained in our asymptotic theory. When $\lambda = 1$, equation (6.52) tells the increment of deformation ratio $D$ as $\alpha$ increases, the asymptotic expansion for slip velocity when $\alpha \neq 1$ makes larger difference between asymptotics and numerics.
Steady state deformation: \((\lambda, \Psi, \alpha) = (1, 1, 1)\)

Asymptotic Deformation
Numerical Deformation

Figure 8.1  Steady state deformation \(D\) as a function of capillary number. The left numerical results show the agreement with leading order small deformation theory for equal conductivity field \((\alpha = 1)\) when the slip velocity is not necessary to be expanded, while the right figure is for \(\alpha = 10\) when the leading order term of slip velocity is applied asymptotically for our theory. Both figures show good match up to \(D \approx 0.05\). The deformation curve for \(\alpha = 10\) departs from the leading order solution quickly for \(Ca > 0.1\), it is caused by the first linear order theory and the approximation in the expansion for the slip velocity.

For chosen set of parameters \((\lambda, \Psi, \alpha) = (1, 1, 1)\), we increase the electrical capillary number to the critical value above which the breakup of the drop happens. The asymptotic work also shows the various of \(\Psi\) does not change the deformation for \(\alpha = 1\) here. Figure 8.2 shows the agreement with leading order theory fails as \(Ca > 0.1\), four numerical generated steady state drop shapes are shown and the deformations for different capillary numbers are presented to be monotonic to the value of capillary number. However, the steady state does not exist any more when the numerical calculations are carried out continuously as \(Ca\) is increased to be greater than a critical value, our numerical observation approximates the critical value for breakup as \(Ca \approx 0.38\) up to second digits. Above that value, a stretching elongation and breakup of the drop is observed, more details about the correlation between this critical value and other parameters will be discussed in later sections. As \(Ca\) is
Figure 8.2  Drop deformation increases as $Ca$ increases until the breakup critical value $Ca = 0.38$, the figure for zooming in tells the good agreement between asymptotic and numerical solutions when $Ca < 0.1$ and four smaller shapes on the top are for $Ca = 0.1, 0.2, 0.3, 0.38$. Above 0.38, no steady state is observed increased from 0.38 to 0.39, Figure 8.3 shows the shape changing process for breakup dependent on time.

8.2 Fluid Motion

Because of the existence of slip velocity across the Debye layer, the flow pattern becomes interesting to study. Recall that we only consider the slip velocity in external field with assumptions, the case will be more complicated when both external and internal slip velocities exist.

The slip velocity needs to be analyzed before summarizing all field flow. In all the following simulations, we use the slip velocity to denote the tangential component
of the slip velocity for simplicity. For the given set of parameters \((\lambda, \Psi, \alpha, Ca) = (1, 1, 1, 0.39)\), \(Ca = 0.21\) is also the critical value for breakup. Figure 8.4 presents the increment of slip velocity near the equator and slight decrement near the poles in order to access the steady state. The slip velocity is zero on the poles and equator, it is continuous and changes direction when crossing the poles, where the positive sign means the velocity direction is clockwise.

The numerical method has been tested to check the convergence or accuracy for the numerical simulation before examining the effects of \(\lambda, \Psi, \alpha\) and \(Ca\). For the same parameters as above, we consider the maximal normal interfacial velocity and relative error of the drop volume as time goes on till the steady state is arrived.
\((\lambda, \Psi, \alpha, \text{Ca}) = (1, 0.1, 10, 0.21)\).

**Figure 8.4** Evolution of the drop deformation (left) and the external slip velocity (right) with given parameters at times \(t = 0:15\), the dash lines are the initial sphere (left) and initial slip velocity (right). \(x\)-label of the right figure is the rescaled arclength by \(L\) (the length of the half boundary curve).

\((\lambda, \Psi, \alpha, \text{Ca}) = (1, 0.1, 10, 0.21)\).

**Figure 8.5** Decreasing maximal normal interfacial velocity and convergent relative error of drop volume.
Figure 8.5 shows the bounded and decreasing maximal normal velocity till it is less than $10^{-4}$, the relative error of the drop volume is convergent and less than $10^{-8}$.

From the boundary integral equation, we can conclude the influence to fluid motion by the slip velocity. Our observation shows that in fixed region the slip velocity has the same direction property for different parameters, however, its numerical value is variable with the effects of $\alpha$ or $\Psi$. Figure 8.6 shows the increasing of slip velocity with fixing $\Psi$ and incrementing $\alpha$, while Figure 8.7 shows the decreasing of slip velocity with fixing $\alpha = 10$ and incrementing $\Psi$. Both numerical solutions are for initial spherical cases which are not related with $\lambda$ and $Ca$. The six different values of each parameter are given in the captions, while three lines in Figure 8.7 with value $\Psi = 0.01, 0.1, 1$ are so close to each other that they appear as the top line in the graph. This is caused by the high order terms with $\Psi$ in asymptotic approximation, which becomes very small as $\Psi < 1$.

![Initial Slip Velocity, $\Psi=1$](image)

**Figure 8.6** Initial slip velocities with $\alpha = .01, .1, .5, 1, 2, 5, 10, 100$, the slip velocity is increasing in the arrow direction for $s/L \in (0, 0.5)$ and decreasing for $s/L \in (0.5, 1)$ as $\alpha$ is increasing.
Figure 8.7  Initial slip velocity with $\Psi = .01, .1, 1, 5, 10, 20, 50$, the slip velocity is decreasing in the arrow direction for $s/L \in (0, 0.5)$ and increasing for $s/L \in (0.5, 1)$ as $\Psi$ is increasing. As $\Psi = .01, .1, 1$, the numerical solutions are pretty close and appear as the top line when $s/L \in (0, 0.5)$ and the bottom line when $s/L \in (0.5, 1)$.

In steady state for the given set of parameters $(\lambda, \Psi, \alpha, Ca) = (1, 20, 10, 0.31)$, where $Ca = 0.31$ is the critical value for this case, the electric and fluid fields within the Debye layer are required to analyze before computing the slip velocity and fluid motion. Profiles for the total electric potential and relative slip velocity data for several chosen nodes on the boundary versus the normal rescaled coordinate $N$ are shown in Figure 8.8. Within the Debye layer, the tangential component of total fluid velocity is the combination of tangential interfacial velocity and slip velocity: $u_t = u_{int} + u_{slip}$. Numerical calculation for the same nodes is also presented in Figure 8.9. As $N$ increases, the total fluid tangential velocity goes to zero and changes its sign, which means the direction of tangential fluid velocity is changed within the debye layer because of the effect coming from the slip velocity. Figure 8.10 compares the values of shear interfacial velocity and slip velocity (as $N \to +\infty$) and gives the numerical summation which is in different sign with the interfacial velocity.
Figure 8.8 In steady state, total electric potential and slip velocity within the debye layer for nodes $s/L = 0 : 1/16 : 1$ on the interface versus the rescaled normal coordinate $N$.

Figure 8.9 In steady state, total tangential fluid velocity within the Debye layer for nodes $s/L = 0 : 1/16 : 1$ on the interface versus the rescaled normal coordinate $N$, the corresponding velocities on these nodes when $N = 0$ are $0.1622$ $0.3018$ $0.3994$ $0.4419$ $0.4240$ $0.3488$ $0.2155$ $0.4240$ $0.4419$ $0.3994$ $0.3018$ $0.1622$ $0$. The velocities change signs before $N = 2$ and converge to finite numbers as $N \to +\infty$. 
Figure 8.10 Combination of tangential interfacial velocity (star line) and relative slip velocity as $N \to +\infty$ (dash line) which gives the total tangential fluid velocity in outer field near the interface (solid line). The opposite sign of total velocity and interfacial velocity shows the opposite flow motion across the interface in outer fields.

Since the axisymmetric drop is also symmetry with respect to the equatorial plane, the one-fourth of the ellipse is studied here. The flow patterns around the initial spherical and the steady state drop are computed numerically by evaluating the velocity field from boundary integral equations, which are shown in Figure 8.11. The initial flow (left) predicts the prolate direction while the steady state flow (right) presents the circulation of fluid flow within the drop. The opposite tangential velocity directions in the outer field when crossing the interface is also observed with the effects of slip velocity as we stated before. Inside the drop for Figure 8.11 (right), no electric field exists in the outer region and no slip velocity exists in the Debye layer, however, the fluid motion does exist. In steady state, we consider that the interface is in normal force equilibrium. Then we can predict the tangential motion by balancing the total electric (electric and osmotic) shear stresses and viscous shear stresses. This is different from the case when one fluid is much more highly conducting than the
Figure 8.11 Initial (left) and steady state (right) fluid motions. The solid lines are the one-fourth of the interfacial curve. The normal velocity predicts the prolate motion of the interface in the initial state (left) until the steady state is arrived (right) when there is only shear flow near the interface, the circulation motion of inside the drop can also be observed.

other and the opposite extreming case when the two fluids are considered as perfectly insulating. In the first case, the interface is perfectly conducting, thus, it supports no tangential electric field, while in the second case there is no free charge density on the surface which only supports perpendicular surface force to the interface and no tangential fluid motion.

More numerical simulations were done for the drop breakup modes in order to determine the critical capillary numbers with the effects of dimensionless surface potential $\Psi$ and conductivity ratio $\alpha$. The primary objective of this part is still to examine the deformation properties with equal viscosities $\lambda = 1$, then we fix one of $\Psi$
Figure 8.12  Critical capillary numbers as a function of $\Psi$ with fixed $\alpha = 10$, and a function of $\alpha$ with fixed $\Psi = 0.1$. The star points in the left figure are for $\Psi = 0.01, 0.1, 1, 5, 10, 20, 50$, when $\Psi < 1$, the critical value appears to be stable as to be 0.21. The star points in the right figure are for $\alpha = 0.01, 0.5, 1, 2, 5, 10$, and the critical capillary value decreases slightly to 0.2 when $\alpha > 10$.

and $\alpha$ and study the behavior with varying the other parameter. Figure 8.12 contains the critical capillary numbers as a function of $\Psi$ with $(\lambda, \alpha) = (1, 10)$ and a function of $\alpha$ with $(\lambda, \Psi) = (1, 0.1)$. As previously mentioned, the numerical solution for $\Psi < 1$ does not vary much, see Figure 8.12(left), the slope decreases as $\Psi$ increases and we expect the critical value will converge to a finite number for this set of parameters. When $\Psi$ is fixed as 0.1, the large deformation as $\alpha$ increases causes the decreasing of critical capillary number, however when $\alpha$ is very small (surrounding fluid is much more highly conducting than the drop), the critical capillary number becomes very large and we expect the drop will never break up as $\alpha$ is quite small, for instance $\alpha < 0.01$. 
8.3 Numerical Simulation with Viscosity Effect

Although we solved all the numerical cases with equal viscosities in previous sections, the effect of viscosity has been included in our previous small deformation analysis, which is matched very well with our numerical simulations for small capillary numbers. Figure 8.13 shows the good match of asymptotic solutions (dash lines) and numerical deformations with respect to different viscosity ratios. For the given set of parameters \((\Psi, \alpha) = (0.1, 10)\), the increasing drop deformation as \(\lambda\) increases is observed. The more linear behavior of deformation ratio \((D)\) versus capillary number \((Ca)\) as \(\lambda\) decreases can also be well explained by the small deformation theory. As \(\lambda\) approaches to zero, small coefficients of high order terms in small deformation theory cause the dominant linear relation. When the viscosity of the drop is dominant
Figure 8.14 Elongating drop till almost cylindrical with no breakup.

over the surrounding flow, we observed the similar deformation as in [8] stated for classical electrohydrodynamics, “the drop undergoes the cascade and becomes almost cylindrical, with bulbous ends”, which is quantitatively explained by the electrohydrodynamic stability analysis in [36] for fluid cylinders in electric fields. Saville stated that the weak electrical fields can completely stabilize the cylinder. For $\lambda = 50$, the deformation ratio increases rapidly (Figure 8.13) and the drop can keep elongating as Figure 8.14 shows for time dependent process.

In the contrast case when the viscosity of the surrounding flow is dominant over the drop, it was found that the critical capillary number for breakup will increase as $\lambda$ decreases, however, for larger capillary numbers the interfacial velocity of the drop increases rapidly and goes to breakup.
CHAPTER 9

TIME DEPENDENT CHARGING PROCESS

The quasi-steady state of charging process was assumed in our previous study because the time scale for charging is much faster than the time scale for fluid motion, however, it is not always true for the large time scale charging process. In this case, to greatly simplify the model, we assume the time scales satisfy the relation $T_C \sim T_F$. In the general model, steady state Laplace equation in outer field can never be used; time dependent matching conditions for inner region and outer region will be applied for solving electric potentials, charge density, slip velocity and interfacial velocity. We present a set of effective equations for the drop deformation problem with time dependent boundary conditions. In order to simulate the deformation accurately and fast, we modified our previous numerical methods and developed new time marching schemes to solve the time dependent problem.

9.1 General Model

The assumption that both Debye lengths are the same is still made here. We only consider the case of equal viscosities in this chapter. Recall the dimensionless Poisson’s equations (2.42, 2.43) and diffusion equations (2.44, 2.45) with leading order solutions for charge density and electric potential within the layers

\[
c(s, N, t)_\pm^0 = C_\pm^0(s, t)e^{-N},
\]

\[
\phi(s, N, t)_+^0 = -C_+^0(s, t)e^{-N} + D_+^0(s, t)N + E_+^0(s, t),
\]

\[
\phi(s, N, t)_-^0 = -\frac{1}{K}C_-^0(s, t)e^{-N} + D_-^0(s, t)N + E_-^0(s, t),
\]

where $s$ is the arclength and $N$ is the rescaled normal direction.
The only difference in solving process comes from the matching of inner and outer solutions. We can’t assume the outer Laplace equation has Neumann boundary condition any more, but we can use the notations $\phi_o^\pm$ and $\frac{\partial \phi_o^\pm}{\partial n^\pm}$ for the exact outer solutions and its normal derivatives to expand $\phi_o^\pm$

$$
\phi_o^\pm(n^\pm \to 0) = \phi_o^\pm(n^\pm = 0) + \epsilon N^\pm \cdot \frac{\partial \phi_o^\pm}{\partial n^\pm}(n^\pm = 0) + \ldots,
$$

where $n^\pm$ are the outward and inward normal directions near the interface before rescaling.

The boundary condition for continuity of potentials (2.72) and matching of inner and outer solutions (2.73, 2.74) with solution (2.71) in Section 2.4 give

$$
\left( \frac{1}{K} + 1 \right) C_0^- = \phi_o^- - \phi_o^+,
$$

and (2.71) also leads the equation

$$
\frac{\partial C_0^0}{\partial t} = -\frac{\partial C_0^-}{\partial t}.
$$

Finally, matching of inner and outer solutions with the $O(\epsilon)$ term shows

$$
\frac{\partial \phi_o^+}{\partial n^+} = \frac{\partial C_0^0}{\partial t}, \quad \frac{\partial \phi_o^-}{\partial n^-} = \frac{1}{K} \frac{\partial C_0^-}{\partial t}.
$$

In next step, the relations between $\phi_o^\pm$ and $\frac{\partial \phi_o^\pm}{\partial n^\pm}$ need to be found from the boundary integral representations for the solutions of Laplace equations both inside and outside the drop.

Laplace equation in ‘+’ region:

$$
\nabla^2 \phi_o^+ = 0.
$$

The strategy here is still to decompose $\phi_o^+ = \phi^\infty + \phi_D$, where $\phi^\infty = -E_\infty x$. Applying the boundary integral representation for $\phi_D$, the formula for $\phi_o^+$ can be obtained after
replacing $\phi_D$ by $\phi_{o+} - \phi^\infty$:

$$
\int_{S}^{P.V.} \phi_{o+}(x) \frac{\partial G(x, x_0)}{\partial n_+} dS(x) - \frac{1}{2} \phi_{o+}(x_0) \\
= \int_{S} G(x) \frac{\partial \phi_{o+}(x, x_0) - \phi^\infty(x, x_0)}{\partial n_+} dS(x) + \int_{S}^{P.V.} \phi^\infty(x) \frac{\partial G(x, x_0)}{\partial n_+} dS(x) - \frac{\phi^\infty(x_0)}{2}.
$$

(9.9)

Laplace equation in $'-'$ region:

$$
\nabla^2 \phi_{o-} = 0.
$$

(9.10)

The direct boundary integral representation is applied to give

$$
\int_{S}^{P.V.} \phi_{o-}(x) \frac{\partial G(x, x_0)}{\partial n_-} dS(x) - \frac{1}{2} \phi_{o-}(x_0) = \int_{S} G(x) \frac{\partial \phi_{o-}(x, x_0)}{\partial n_-} dS(x).
$$

(9.11)

The numerical schemes will be formulated later based on the boundary integral equations with time dependent boundary conditions.

### 9.2 Time Dependent Small Deformation Theory

To check the numerical results, we developed the time dependent small deformation theory for time dependent charging problem. The theory can be well used to show the interesting motion of the interface.

We follow the general small deformation theory for the faster charging time case, however, the slip velocity in inner region has been taken into account and both velocities are time dependent. The assumption that potential fields and velocity fields are solved for an approximated spherical drop is used here but time dependent boundary conditions are considered. The same expansion with harmonic polynomials for drop interface, the evolution equation and expansion for fluid velocities are applied here.
The time dependent potential field has been solved for a spherical drop in (2.91-2.98). We list some useful properties here based on these potentials:

\[
\phi_o^+ = \left( \frac{3}{2} - \frac{3K}{2(1 + K)} e^{-\frac{2(1+K)}{2K+K^2}t} \right) \cos \theta = f_{b+}(t) \cos \theta, 
\]

\[
\phi_o^- = \frac{3}{2 + K} e^{-\frac{2(1+K)}{2K+K^2}t} \cos \theta = f_{b-}(t) \cos \theta, 
\]

\[
\frac{\partial \phi_o^+}{\partial n_+} = \frac{3K}{2 + K} e^{-\frac{2(1+K)}{2K+K^2}t} \cos \theta = f_{d+}(t) \cos \theta, 
\]

\[
\frac{\partial \phi_o^-}{\partial n_-} = -\frac{3}{2 + K} e^{-\frac{2(1+K)}{2K+K^2}t} \cos \theta = f_{d-}(t) \cos \theta, 
\]

\[
\phi_s = \frac{3}{2(1+K)} \left( \frac{K}{2 + K} e^{-\frac{2(1+K)}{2K+K^2}t} + 1 \right) \cos \theta = f_c(t) \cos \theta, 
\]

\[
\eta^+|_{N=0} = \phi_s - \phi_o^+ = \frac{3K}{2(1 + K)} \left( e^{-\frac{2(1+K)}{2K+K^2}t} - 1 \right) \cos \theta = f_{a+}(t) \cos \theta, 
\]

\[
\eta^-|_{N=0} = \phi_s - \phi_o^- = \frac{3}{2(1 + K)} \left( -e^{-\frac{2(1+K)}{2K+K^2}t} + 1 \right) \cos \theta = f_{a-}(t) \cos \theta, 
\]

\[
v_{slip+} = (\phi_s - \phi_{\infty+}) \frac{\partial \phi_{\infty+}}{\partial s} = -f_{a+}(t) f_{b+}(t) \sin \theta \cos \theta, 
\]

\[
v_{slip-} = -\frac{\alpha}{\lambda}(\phi_s - \phi_{\infty-}) \frac{\partial \phi_{\infty-}}{\partial s} = \frac{\alpha}{\lambda} f_{a-}(t) f_{b-}(t) \sin \theta \cos \theta, 
\]

\[
\frac{\partial v_{slip+}}{\partial s} = -f_{a+}(t) f_{b+}(t) \cos 2\theta, 
\]

\[
\frac{\partial v_{slip-}}{\partial s} = \frac{\alpha}{\lambda} f_{a-}(t) f_{b-}(t) \cos 2\theta, 
\]

where \(v_{slip\pm} = v_{slip\pm} \cdot t\), \(t\) is the tangential direction which is clockwise for a spherical drop.

Before presenting the adjusted stress balance equation, we need to analyze the Stokes equations within the Debye layers. We notice the difference when solving the leading problem for the third component of Stokes equation (5.20). Because the leading order \(O(\frac{1}{\epsilon^2})\) term coming from the third component of \(-\nabla^2 \eta \nabla \phi_o\) (dropping \('+' signs\) is

\[
\frac{\partial^2 \eta}{\partial N^2} \cdot \frac{\partial \phi_o}{\partial n} 
\]

\[ (9.23) \]
for time dependent case, the leading order term coming from $\nabla P$ has to be $O(\frac{1}{\epsilon^2})$, which requires the expansion for pressure

$$P = P_{-1}\epsilon^{-1} + P_0 + \cdots.$$  \hfill (9.24)  

With noticing that the leading order term coming from the third component of $\nabla^2(U + u)$ is $O(\frac{1}{\epsilon})$, we have the following leading order equation $O(\frac{1}{\epsilon^2})$

$$\frac{\partial P_{-1}}{\partial N} = \frac{\partial^2 \eta}{\partial N^2} \frac{\partial \phi_o}{\partial n}.$$  \hfill (9.25)  

The similar solution to (5.42) for above equation is

$$\left( P_{-1+} - \frac{\partial \eta_+}{\partial N} \frac{\partial \phi_{o+}}{\partial n} \right)_{N=+\infty} = \left( P_{-1+} - \frac{\partial \eta_+}{\partial N} \frac{\partial \phi_{o+}}{\partial n} \right)_{N=0} = H_+(\xi_1, \xi_2).$$  \hfill (9.26)  

Similarly, the solution for '$-$' region is

$$\left( P_{-1-} - \alpha \frac{\partial \eta_-}{\partial N} \frac{\partial \phi_{o-}}{\partial n} \right)_{N=+\infty} = \left( P_{-1-} - \alpha \frac{\partial \eta_-}{\partial N} \frac{\partial \phi_{o-}}{\partial n} \right)_{N=0} = H_-(\xi_1, \xi_2).$$  \hfill (9.27)  

In order to balance the $O(\frac{1}{\epsilon})$ term, we have the same equation as (5.40) which is

$$\frac{\partial P_0}{\partial N} = \frac{\partial^2 w_0}{\partial N^2},$$  \hfill (9.28)  

the solutions of this equation are shown in (5.42, 5.43).

The similar procedure to fast charging time case is applied here to present the adjusted stress balance equation

$$[T_{Ho} \cdot n]^+ = [T_H \cdot n]^+ + (T_{Ho+} \cdot n - T_{H+} \cdot n) - (T_{Ho-} \cdot n - T_{H-} \cdot n) = \frac{2\kappa n}{Ca}.$$
\[ - \frac{1}{2} \left[ \frac{1}{l_1^2} \left( \frac{\partial \eta_1}{\partial s} \right)^2 \left( \frac{\partial \phi_+}{\partial s} \right)^2 \right] + \frac{1}{l_2^2} \left( \frac{\partial \eta_2}{\partial s} \right)^2 \left( \frac{\partial \phi_+}{\partial s} \right)^2 \right] \bigg|_{N=0} + \ldots \]

\[ + \left[ \frac{\alpha}{l_1^2} \frac{\partial \phi_1}{\partial n} \frac{\partial \phi_-}{\partial n} \right] \bigg|_{N=0} + \ldots \lambda \left( \frac{\partial w_0}{\partial N} \big|_{N=0} - \frac{\partial w_0}{\partial N} \big|_{N=\infty} \right) + \frac{1}{2} \alpha \left( \frac{\partial \phi_0}{\partial n} \right)^2 \bigg|_{N=0} + \ldots \] (9.29)

Some of the effects of potentials in stress balance equation (9.29) are expressed as follows:

\[ f_{s1}(t, \theta) = \frac{1}{2} \left[ \left( \frac{\partial \eta_+}{\partial s} \right)^2 - \left( \frac{\partial \phi_+}{\partial s} \right)^2 \right] \bigg|_{N=0} + \frac{\partial v_{\text{slip}+}}{\partial s} + \frac{1}{2} \left( \frac{\partial \phi_+}{\partial n} \right)^2 \]

\[ = \frac{1}{2} \left( f_{a+}^2 - f_{c+}^2 \right) \sin^2 \theta - f_{a+} f_{b+} \cos 2\theta + \frac{1}{2} f_{d+}^2 \cos^2 \theta, \] (9.30)

\[ f_{s2}(t, \theta) = \frac{1}{2} \alpha \left[ \left( \frac{\partial \eta_-}{\partial s} \right)^2 - \left( \frac{\partial \phi_-}{\partial s} \right)^2 \right] \bigg|_{N=0} + \lambda \frac{\partial v_{\text{slip}-}}{\partial s} + \frac{1}{2} \alpha \left( \frac{\partial \phi_-}{\partial n} \right)^2 \]

\[ = \frac{1}{2} \alpha \left( f_{a-}^2 - f_{c-}^2 \right) \sin^2 \theta + \alpha f_{a-} f_{b-} \cos 2\theta + \frac{1}{2} \alpha f_{d-}^2 \cos^2 \theta. \] (9.31)

With the multipole representation of fluid velocities (6.13, 6.14) and the equation for velocity:

\[ \mathbf{v}_+ - \mathbf{v}_{\text{slip}+} = \mathbf{v}_- - \mathbf{v}_{\text{slip}-}, \ r = 1, \] (9.32)

we obtain the relation of coefficients:

\[ c_{20}^+ = \frac{2}{3} \sqrt{\frac{6\pi}{5}} f_{a+} f_{b+} = c_{20}^- = \frac{2}{3} \sqrt{\frac{6\pi}{5}} \alpha f_{a-} f_{b-}, \] (9.33)

\[ c_{j0}^+ = c_{j0}^-, \ j > 2, \] (9.34)

\[ c_{j2}^+ = c_{j2}^-, \ j \geq 2. \] (9.35)
The stress balance equation (9.29) gives the different equations from the faster charging time case, which are

\[ \tau_{20}^+ - \lambda \tau_{20}^- = 2 \sqrt{\frac{6\pi}{5}} f_{r0}(t), \]  
(9.36)

\[ \tau_{22}^+ - \lambda \tau_{22}^- = \frac{4}{Ca} f_2 + \frac{4}{3} \sqrt{\frac{\pi}{5}} f_{r2}(t), \]  
(9.37)

where

\[ f_{r0}(t) = f_c(t)(\alpha f_+ - f_d^+), \]  
(9.38)

\[ f_{r2}(t) = \frac{1}{2}(f_{a+}^2(t) - f_c^2(t)) - \frac{\alpha}{2}(f_{a+}^2(t) - f_c^2(t)) + 2(f_{a+}(t)f_b(t) + \alpha f_a(t)f_b(t)) \]
\[ + \frac{1}{2}(-f_{d+}^2 + \alpha f_d^2). \]  
(9.39)

Similarly, we apply equations (6.29 - 6.32) into (9.36) and (9.37) with utilizing the equations (9.33 - 9.35). The result is plugged into the kinematic equation (6.16) to get the leading order time dependent ordinary differential equation

\[ \frac{\partial f_2(t)}{\partial t} + C_1 f_2(t) = C_2(Q_2 e^{-2C_3t} + Q_1 e^{-C_3t} + Q_0), \]  
(9.40)

where

\[ C_1 = \frac{40(\lambda + 1)}{(38\lambda^2 + 89\lambda + 48)Ca}, \]  
(9.41)

\[ C_2 = -\frac{10(\lambda + 1)}{(38\lambda^2 + 89\lambda + 48)} \sqrt{\frac{\pi}{5}}, \]  
(9.42)

\[ C_3 = \frac{2(1 + K)}{2 + K}, \]  
(9.43)

\[ Q_0 = -\frac{9K(2\lambda + 1) + 3(\lambda + 1)}{2(1 + K)(1 + \lambda)}, \]  
(9.44)

\[ Q_1 = -\frac{3(K^2 - \alpha)}{(1 + K)^2} - \frac{3(1 - \alpha)K}{(1 + K)^2(2 + K)} - \frac{9(2 + 3\lambda)}{5(1 + \lambda)} \frac{(\alpha + K)}{(1 + K)(2 + K)} \]
\[ + \frac{3(4 + 7\lambda)}{2(1 + \lambda)} \frac{K}{(1 + K)^2} + \frac{3(1 + 4\lambda)}{1 + \lambda} \frac{\alpha}{(1 + K)(2 + K)}, \]  
(9.45)

\[ Q_2 = \frac{3(K^2 - \alpha)}{2(1 + K)^2} + \frac{3(\alpha - 1)K^2}{2(1 + K)^2(2 + K)^2} - \frac{9(2 + 3\lambda)}{5(1 + \lambda)} \frac{K(\alpha + K)}{(1 + K)(2 + K)^2} \]
\[ - \frac{3(4+7\lambda)}{2(1+\lambda)} \frac{K^2}{(1+K)^2} - \frac{3(1+4\lambda)}{1+\lambda} \frac{\alpha}{(1+K)(2+K)} + \frac{6(\alpha-K^2)}{(2+K)^2}. \] (9.46)

The solution with initial spherical shape is

\[ f_2(t) = C_2 \left[ \frac{Q_2}{C_1 - 2C_3} \left( e^{-2c_3t} - e^{-c_1t} \right) + \frac{Q_1}{C_1 - C_3} \left( e^{-c_3t} - e^{-c_1t} \right) + \frac{Q_0}{C_1} (1 - e^{-c_1t}) \right]. \] (9.47)

As a check, we take \( t \to +\infty \) for the steady state, the above formula gives

\[ f_2(+\infty) = C_2 \frac{Q_0}{C_1} = \frac{9K(2\lambda+1) + 3(\lambda+1)}{8(1+K)(1+\lambda)} \sqrt{\frac{\pi}{5}} Ca, \] (9.48)

which is the same as the faster charging time case (6.51) when \( t \to +\infty \).

## 9.3 Numerical Schemes

The problem we wish to solve consists of the boundary integral equation for potential field (9.9, 9.11), interfacial velocity (4.25) and the kinematic condition (7.7) for updating interface.

The idea of the straightforward, time-marching scheme for solving the concentration for updated surface was first proposed in [6] for surfactant problem. We apply the same idea here for computing the charge density. To describe the main schemes more clearly, we list the sequence of steps as follows:

1. For a given or simulated shape at time \( T \), with known initial conditions for \( c_\pm^0(s, N, t) \) and \( \phi_\pm(s, N, t) \), we can solve the time dependent ODEs for \( c_\pm^0 \) and the boundary integral equations for \( \phi_\pm, \partial \phi_\pm / \partial n_\pm \). Since the ODEs are also dependent on the shape of the drop, it has to be solved at each time step, we denote \( c_\pm^0(s, N, t = 0) \) as the initial condition for time \( T \) and \( c_\pm^0(s, N, t = \Delta t) \) as the charge density at time \( T + \Delta t \). The interfacial velocity \( u_n \) can be solved numerically by boundary integral equations with known \( \phi_\pm \). More details about these schemes will be discussed later.

2. At time \( T + \Delta t \), we shall have updated the drop shape by integrating the kinematic boundary condition. The updated charge density \( c_\pm^0(s, N, t = \Delta t) \) is used as
initial condition for the new time dependent ODEs for the charge density $\tilde{c}_\pm^\rho(s,N,t)$, where $\tilde{c}_\pm^\rho(s,N,t=0) = c_\pm^\rho(s,N,t = \Delta t)$ and $\tilde{c}_\pm^\rho(s,N,t = \Delta t)$ is used as next initial condition. Potential fields can be solved then and be applied for computing interfacial velocity to update the drop shape.

(3) New shape is obtained, return to (1) repeatedly.

During the numerical procedure, we made two main approximations. The first one, which is also used before for the faster charging time scale case, is that we assume the velocity field during time from $T$ to $T + \Delta t$ is well approximated by the velocity field at time $T$. The second approximation is for the ion charge density. When computing the charging process, we assume the drop shape during time from $T$ to $T + \Delta t$ is well approximated by the shape at time $T$. Both approximations are not exactly correct but are shown to be well convergent to analytic solutions with checking convergence and comparing to small deformation theory.

We simplify the representation formula for boundary integral equations (9.9, 9.11) as

$$
\begin{align*}
(U - \frac{1}{2}I) \phi_{o+} &= V \frac{\partial \phi_{o+}}{\partial n_+} + w, \\
(-U - \frac{1}{2}I) \phi_{o-} &= V \frac{\partial \phi_{o-}}{\partial n_-},
\end{align*}
$$

for simplicity, we denote $\phi_{o\pm}$ and $\frac{\partial \phi_{o\pm}}{\partial n_\pm}$ as vectors for all nodes on the boundary, and the vector $w$ has the expression $w = [w(1)\ w(2)\ \cdots]$, 

$$
w(i) = \int_{S}^{P.V.} \phi^\infty(x) \frac{\partial G(x,x_i)}{\partial n_+} dS(x) - \frac{\phi^\infty(x_i)}{2},
$$

which can be evaluated explicitly for given shape and nodes on the boundary. Recall that matrices $U, V$ depend on the drop shape and are all time dependent.
With conditions (9.5 - 9.7), we are able to combine (9.49, 9.50) to get the time dependent ODEs for $C_0^0(t)$

$$(K + 1)C_0^0(t) = \left[ K \left( U - \frac{1}{2} I \right)^{-1} + \left( -U - \frac{1}{2} I \right)^{-1} \right] V \frac{\partial C_0^0(t)}{\partial t} - K \left( U - \frac{1}{2} I \right)^{-1} \mathbf{w},$$

(9.52)

where $C_0^0(t)$ is a vector for all discretized nodes, i.e., $C_0^0(t) = [C_0^0(s_1, t) \ C_0^0(s_2, t) \cdots]$. Charge density can be evaluated by solving the ODEs with initial conditions. Time derivatives of $C_0^0$ are utilized for equation (9.7) to solve normal derivatives of potentials, which can be applied into boundary integral equations (9.49) and (9.50) to solve outer potential fields.

### 9.4 Numerical Results

In this section, we quantify the effects of factors known to be important. To characterize the effects of diffusion layer on drop deformation, we have to consider the electric capillary number ($Ca$), dimensionless surface potential ($\Psi$), property ratios of conductivities ($K$), permittivities ($\alpha$) and viscosities ($\lambda$). The permittivities’ ratio is still set to be equal to conductivities’ ratio. The obvious quantitative effect from permittivity can be shown from the boundary condition and two terms of the modified boundary integral equation (4.25). The first part is the slip velocity field in ‘$-$’ region which is always existing till steady state is arrived, it is also related with permittivity by the analysis for inner Stokes equations; the second part comes from the force jump including the potential field in ‘$-$’ region which can be shown in (9.29).

In this section, we fix $\lambda$ at unity for reducing computational costs. The effect of viscosity ratio is similar as we discussed before in the case for fast charging time scale. $\Psi$ is held as a small number, i.e., $\Psi = 0.1$. When the parameter $K$ is very large, which means the drop is much more highly conducting than the surrounding fluid, the relaxation time in the drop is short compared to that in the surrounding fluid and other dynamical times. The drop can be regarded as perfectly conducting with equal
potentials, thus, the $'-'$ region can be thought to support no effect to the deformation. It also supports no tangential stress on the surface because of the equal potentials. The only term matters is the tangential derivative of excess potential which is very small at the beginning. In conclusion, we can not get significant interfacial velocity for very large conductivity ratio $K$, so we choose $K \leq O(1)$ in this section. When $\alpha$ is very small, the effect of electric field in $'-'$ region is smaller compared to that in $'+'$ region; that is, the effect of permittivity can be neglected, and the drop will deform in the same direction as the previous faster charging time case. When $\alpha$ is close to unity, at early time, the effects of both $'+'$ and $'-'$ regions are canceled and very small interfacial velocity is observed. Because of the assumption that Debye lengths inside and outside the drop are equal to each other, we still fix $\alpha = K$ and relax this assumption in the future.

Figure 9.1 Drop deformation shape for small times and steady state (right bottom).
The slip velocity in the $'-'$ region needs to be included in the numerical simulation for fluid velocity, which is different from the case before. In the following parts, small deformation results are still used for checking the numerical calculation. Different drop deformations are observed and explained both analytically and physically.

9.4.1 Small Deformation and Steady State

![Figure 9.2](image_url) Drop deformation ratio versus time.

For given set of parameters in Figure 9.1, both small deformations at small times and the steady state deformation are presented. For more quantitative discussion, Figure 9.2 also shows the drop deformation ratio versus time, where $D < 0$ means the drop is oblate and $D > 0$ means it’s prolate. Both numerical and analytical solutions show that the drop deforms into a prolate shape till the steady state. The good match is observed for small deformation when time is small or steady state is arrived.
9.4.2 Large Deformation and Breakup

In this section, we study the large drop deformation with changing the electric field or other parameters. By our small deformation theory, the drop always deforms into a prolate shape when we set $\alpha = K$. The oblate shape is expected when we relax the assumption that $\alpha = K$, however, no numerical results are presented here.

The deformation direction is similar as the case for quasi-steady state charging process, thus, we will only show two numerical examples here and save other interesting deformations for our future work. The first example is for the case $(\lambda, \Psi, K, \alpha, Ca) = (1, 0.1, 10, 10, 0.2)$, the conductivities’s ratio is increased to 10, our simulation results show that the drop deforms into a prolate shape and arrives at the steady state (Figure 9.3).

$$(\lambda, \Psi, K, \alpha, Ca) = (1, 0.1, 10, 10, 0.2).$$

![Figure 9.3](image-url)

**Figure 9.3** Drop deformation shape *versus* time.

The second example is for $\alpha = K = 5$. When $Ca$ is increased, no steady state is observed since the strong electric field. Figure 9.4 shows that the instability appears with the fast evolving fingers at the drop tips and the drop breaks up, which is similar
as observed in [8] in some cases. We also observe less deformation and fatter drop profile near the poles compared with the very elongated and almost cylindrical shape for the case of fast charging time scale (Figure 8.3).

$$(\lambda, \psi, K, \alpha, Ca) = (1, 0.1, 5, 5, 1).$$

Figure 9.4 Drop deformation shape *versus* time.
CHAPTER 10

CONCLUSIONS

10.1 Summary

In this thesis, we have presented a fast and accurate ‘hybrid’ or multiscale numerical method for the full moving boundary problem in 3D axisymmetric geometries. We have developed the asymptotic method for ‘induced-charge electro-kinetic flow’ and adjusted boundary integral representations for simulating the fluid flow.

In our model, a thin Debye layer and a strong slip flow near the interface have been considered. The complex fluid dynamics in the Debye layer are also studied. We solve the leading order problem for the electric field within the layers and use asymptotic methods to match the outer Stokes fields. Small deformation theory is developed for our model, which has been utilized to predict the small deformation and check the numerical simulations. Two cases which have been discussed in our work are:

\[ T_C \ll T_F \]. Charging time is much faster than the fluid motion time. We solve the Poisson-Boltzmann equation within the layer to obtain the quasi-steady state charge density and apply it into our adjusted boundary integral method to compute the fluid flow and update the drop profile. Analytic solution can be obtained here for electric fields within the layer, which makes our numerical process have low complexity.

\[ T_C \sim T_F \]. Charging time is similar to the fluid motion time. We solve the time dependent system with Poisson’s equation and electrokinetic equations within the layer. Because of the dependence on the drop shape, we have to compute the numerical solution for charge density at each time step with more complexity compared to the previous case. Our numerical method for the previous case is adaptive and can be used here to simulate the fluid flow and update the drop profile.
We have developed both steady state and time dependent small deformation theories. We first solve the leading order problems for both electric fields and fluid fields, then apply them into the kinematic boundary condition and stress balance equations. These two theories are used to check the numerical solutions in the corresponding cases.

10.2 Future Work

Steric effects in the dynamics. We have focused on the drop deformation with considering the ‘induced-charge electro-kinetic’ flow. However, we assume the electrolytes of point charges and ignore the steric effects. With considering the finite size of ions, we have to use modified Poisson-Boltzman equation and identify the new features of the more complex dynamics within the Debye layer. We have to construct new model for ions with finite size and compare the steric effects with our previous work.

Directed motion and morphological transitions of vesicles We have achieved good understanding with drop interface in our previous work. Another direction of the extensions is to study the model for vesicles, which have more complex mechanics. For instance, the vesicle area is constant and it is area incompressible. What is more, within the applied electric field in electrolytes, the lipid membrane acts as a charging capacitor. The capacitive force needs to be considered for force balance on the boundary. More challenges have to be solved for numerical simulations. We can start the extension by constructing a simple model for vesicles.

Fast and accurate boundary integral numerical method for drop elongation. In our previous work, we have used equal arc-length points on the boundary for numerical simulation. For small number of points, the computation cost is low for
our axisymmetric model. However, this does not work very well for high-curvature tips. A classical solution is to adjust the location of fixed number of points due to the curvature of the surface. Because of the lack of experimental data, and the numerical error for this approach which has not been proved completely, in order to maintain the accuracy of the numerical method, we can increase the number of points and develop fast numerical methods to reduce computation cost for huge number of points.
The clamped-end cubic splines method gives us a linear system with a tridiagonal matrix. Thomas’ algorithm would be a good choice to solve the system. However, in our problem, other coefficients including the form with multiplication of matrices such as $A \cdot B^{-1} \cdot C$ need to be evaluated. Thus, in order to compute the coefficient matrices $A$, $B$ and $C$ in the cubic-splines representations (7.3) and (7.4), we need to solve the inverse of the tridiagonal matrix $T$:

$$T = \begin{bmatrix}
    a_1 & b_1 \\
    c_1 & a_2 & b_2 \\
    & c_2 & \ddots & \ddots \\
    & & \ddots & \ddots & b_{N-1} \\
    & & & c_{N-1} & a_N
\end{bmatrix}. \quad (A.1)$$

To reduce the computational cost of evaluating the inverse, we use the analytic solution in [37]. The inverse of the matrix $T$:

$$T_{ij}^{-1} = \begin{cases}
    (-1)^{i+j} b_i \cdots b_{j-1} \theta_{i-1} \phi_{j+1}/\theta_{N+1}, & \text{if } i \leq j, \\
    (-1)^{i+j} c_j \cdots c_{i-1} \theta_{j-1} \phi_{i+1}/\theta_{N+1}, & \text{if } i > j,
\end{cases} \quad (A.2)$$

where

$$\theta_i = a_i \theta_{i-1} - b_{i-1} c_{i-1} \theta_{i-2}, \quad \text{for } i = 2, \ldots, N + 1, \quad (A.3)$$

$$\theta_0 = 1, \quad \theta_1 = a_1, \quad (A.4)$$

$$\phi_i = a_i \phi_{i+1} - b_i c_i \phi_{i+2}, \quad \text{for } i = N, \ldots, 1, \quad (A.5)$$

$$\phi_{N+2} = 1, \quad \phi_{N+1} = a_{N+1}, \quad (A.6)$$

$$\theta_{N+1} = \det T. \quad (A.7)$$
The computational cost then becomes the multiplication of matrices.
APPENDIX B

FREE SPACE AXI-SYMMETRIC KERNEL FOR LAPLACE EQUATION

The free-space axisymmetric Green’s function:

\[
G_{AX}(x, y, x_0, y_0) = \frac{1}{4\pi} \int_0^{2\pi} \frac{du}{[(x-x_0)^2 + (y+y_0)^2 - 4yy_0\cos^2 u]^{1/2}} \\
= \frac{F(k)}{\pi\sqrt{(x-x_0)^2 + (y+y_0)^2}},
\]

where \(F(k)\) is the complete elliptic integral of the first kind with logarithmic behavior as \(x\) tends to \(x_0\) and \(y\) tends to \(y_0\). With noticing

\[
k^2 = \frac{4yy_0}{(x-x_0)^2 + (y+y_0)^2},
\]

when \(y_0 \neq 0\), the weakly singular limit is

\[
G_{AX}(x, y, x_0, y_0) \approx -\frac{1}{2\pi y_0} \ln \sqrt{(x-x_0)^2 + (y-y_0)^2},
\]

also, we can obtain weakly singular part for double layer potential

\[
\frac{\partial G_{AX}}{\partial n} = -\frac{x_s}{4\pi y^2} \left[ \ln 4\sqrt{(x-x_0)^2 + (y+y_0)^2} - \ln \sqrt{(x-x_0)^2 + (y-y_0)^2} \right],
\]

where \(x_s\) means the derivative with respect to arclength \(s\), however, when \(y_0 = 0\), the integrands for both single and double layers as \(x\) tends to \(x_0\) and \(y\) tends to 0 are smooth, we have shown the regular behaviors:

\[
y \cdot G_{AX}(x, y, x_0, 0) = \frac{1}{2 \sqrt{1 + \left(\frac{x}{y_s}\right)^2}},
\]

\[
y \cdot \frac{\partial G_{AX}(x, y, x_0, 0)}{\partial n} = \frac{y^2x_{ss} - y_s y_{ss} x_s}{4 \left[ x_s^2 + y_s^2 \right]^{3/2}}.
\]


