

PART II: ELECTROSTATICS ASPECTS: MODELING, APPROXIMATIONS AND GEOMETRY

Chapter III. Principles of Applied Electrical Field

3.1 Introduction and Motivation

Scientists have long known that electrical fields affect the movement of fluids and that proper arrangement of direction and intensity may influence the desired results of applications where flow and solute transport are meant to be controlled (Saville et. al. 1989; Todd, 1990; Acar et. al. 1995; Yeung et. al. 1997; Virkutyte et. al. 2002). Typical examples of movement mechanisms that are triggered by electrical fields are electroosmosis, electromigration, and electrophoresis (Hiemenz and Rajegollalau, 1996; Saville et. al. 1980; Hunter, 1935; Graves, 1988; Ivory, 1988, 1990; Ho et. al., 1997, Langeman, R., 1993; Chilingar et. al., 1997). The first, electroosmosis, is considered one of the most important electro-mechanisms in that it induces hydraulic movement. In fact, electroosmosis is sometime so over emphasized that researchers and practitioners neglect to consider other driving forces. Nevertheless, given the proper weight, electroosmosis has been related to the electrostatic potential. For this reason, in every electrokinetic related application, the electrostatic potential is a key function to be identified in order to understand its effect on flow regimes. To better visualize this dependency, a simplified version of the momentum equation is presented next with electroosmosis as the only driving force.

$$\mu \cdot \frac{\partial^2 V_x}{\partial y^2} = -\rho_e(\psi) \cdot E_x \quad (3.1)$$

where μ is viscosity, V_x is the axial velocity, “y” is the transversal coordinate, ρ_e is the density of charge, Ψ is the electrostatic potential, and E_x is the applied electrical field.

In the left side hand of equation 3.1 the viscous force, expressed as a differential of velocity according to Newton’s law, balances the electroosmotic force, expressed in the right side hand of the same equation (Probstein, 1994). The $\rho_e(\psi)$ term is a function of the electrostatic potential, Ψ . Although, more details about this functionality are given in next chapters, equation 3.1 demonstrates the relationship between the electrostatic potential, Ψ , and the hydrodynamic velocity, V_x .

To describe flow and its related transport phenomena, triggered by electrostatic potential, a common practice is the development of a model that includes the electrostatic term when describing a particular system as in equation 3.1. This is followed by the mathematical solution of the all related dependent variables. Once this has been accomplished, the influence of the electrostatic potential on its dependent variables can be assessed. In this process, the ability to accurately describe or predict the electrical potential is a key factor to study the electro-mechanism effects on, for example, hydrodynamic velocity, solute concentration or temperature. Subsequently, for these complex transport phenomena, where electrical fields represent an additional driving force, an even better description of the electrostatic potential as function of its location is required to successfully determine its influence on other dependent variables of interest such as velocity and temperature (Turk and Ivory, 1984; Gebhart et. al., 1988; Bosse, 1998).

Following the argument of the previous paragraphs, it is clear that having an explicit mathematical expression for the electrostatic potential is very much desired. In addition, such expressions should describe the geometries that are under study in the present work. In consequence, the following sections are dedicated to analyze the basis of the electrostatic potential and to derive meaningful analytical expressions to be used in the development of this thesis. The effort is also necessary if an important contribution is to be made on the subject. In particular, chapter IV is devoted to that task as the present chapter is to establishing the foundations.

3.2 The Role of Geometry

Deriving an explicit mathematical expression for the electrostatic potential is not necessarily easy to accomplish. As temperature, in non-isothermal systems, is part of a more complex differential expression such as the heat transfer continuity equation, the response of an ion to an electrical field is defined by the Poisson's equation (Probstein, 1994). This expression is as follows.

$$\nabla^2\psi = -\rho_e / \varepsilon \quad (3.2)$$

where ε is the media permittivity.

In right hand side of equation 3.2 appears the term density of charge, ρ_e , described previously. This term accounts for ions flux and distribution. The usual convention is considering that the ions behave as described by Boltzmann. The assumption yields a non-linear differential equation which is the common starting point for the description of the electrostatic potential; this is the Poisson-Boltzmann equation (Probstein, 1994; Hiemenz and Rajegollalau, 1996).

$$\nabla^2\psi = \lambda^2 \sinh \psi \quad (3.3)$$

where λ is the inverse Debye length.

The reason equation 3.3 is a non-linear differential equation is that in its right hand side the hyperbolic sine function (that is related to the free charge density) is present. A very common simplification invokes the Debye Hückel approximation usually written as $\sinh \psi \approx \psi$ which converts the Poisson-Boltzmann equation in the following linear expression (Probstein, 1994).

$$\nabla^2 \psi = \lambda^2 \psi \quad (3.4)$$

In terms of the geometries that this study concentrates on, equation 3.4 must be solved for a planar, cylindrical and annular system. Therefore, the main focus of the next subsection is to develop the mathematical expressions yielded by the Debye Hückel approximation of the Poisson-Boltzmann differential equation for the mentioned geometrical systems.

3.2.1 Capillary System in a Planar Geometry

The system under analysis is shown in Figure 3.1. This system consists of two parallel walls, each subjected to a dimensionless electrostatic potential equal to Ψ^*_w . In order to take advantage of the symmetry, the coordinates have been placed in the vertical center of the capillary domain. In dimensionless coordinate, the wall located at the right hand side is at the location $\xi=1$ while the one on the left hand side is at $\xi=-1$, where ξ is the dimensionless transversal coordinate.

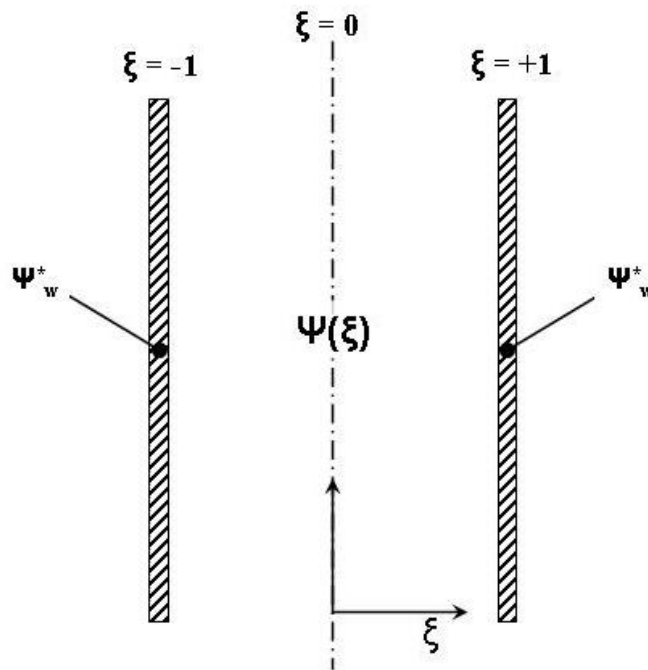


Figure 3.1 Geometrical sketch of a planar capillary channel and coordinate system

In term of the electrostatic forces, the system is defined by Equation 3.3 jointly with appropriate boundary conditions. When applied, the Debye-Hückel approximation yields following differential model.

$$\frac{d^2\psi}{d\xi^2} = \lambda^2 \cdot \psi \quad (3.5a)$$

$$\psi \Big|_{\xi=-1} = \psi_w \quad @ \quad \xi = -1 \quad (3.5b)$$

$$\frac{d\psi}{d\xi} \Big|_{\xi=0} = 0 \quad @ \quad \xi = 0 \quad (3.5c)$$

$$\psi \Big|_{\xi=+1} = \psi_w \quad @ \quad \xi = +1 \quad (3.5d)$$

To solve the system represented by equation 3.5 three boundary conditions are required. The electrostatic potential in the domain $-1 \leq \xi \leq +1$ is found between two parallel walls. Each wall is affecting the fluid with a zeta-potential of Ψ_w . In consequence, the net electrostatic potential is made of the simple addition of both effects. Therefore, equation 3.5 a must be solved for two sets of boundary conditions; this is for the boundary conditions on the left hand side, equation 3.5 b&c, and for the boundary conditions on the right hand side, equation 3.5 c&d. The respective solutions must be added. In such a derivation and for coordinate system shown in figure 2, the obtained analytical solution of the model described by equations 3.5a-d is given by the following expression.

$$\psi(\xi) = 2 \cdot \psi_w \cdot \frac{\text{Cosh}(\lambda \cdot \xi)}{\text{Cosh}(\lambda)} \quad (3.6)$$

where Ψ is the dimensionless electrical potential, ξ the dimensionless transversal coordinate and λ the dimensionless inverse Debye length.

3.2.2 Capillary System in a Cylindrical Geometry

The sketch of the system under analysis is shown in Figure 3.2. Such a system consists of cylindrical capillary whose walls are subjected to a dimensionless electrostatic potential equal to Ψ_w . The intrinsic symmetry of the system conveniently suggests setting the coordinates at the center of the capillary domain. In dimensionless coordinates, the center of the system is at the location $\xi=0$ while the wall of the capillary is located at $\xi=+1$ for the positive domain.

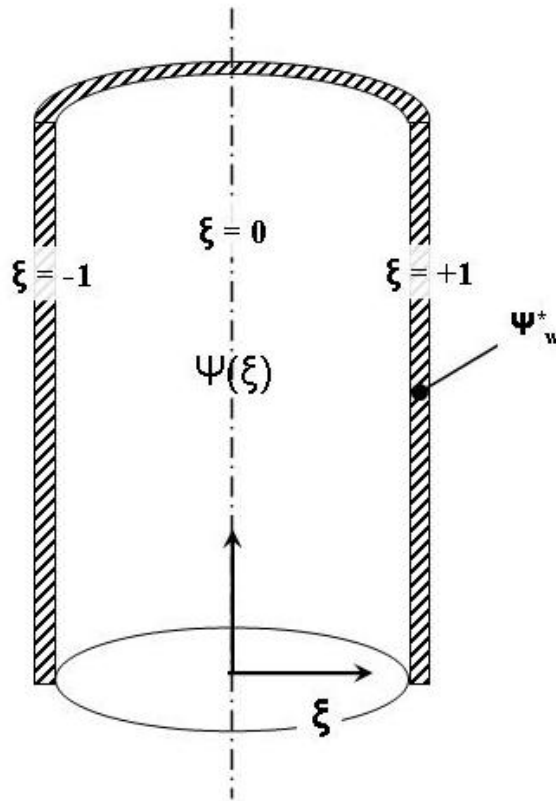


Figure 3.2 Geometrical sketch of a cylindrical capillary channel and coordinate system

As in the previous case, in terms of the electrostatic force, the system is defined by equation 3.3 and the proper boundary conditions. The Debye-Hückel approximation reduces

this expression and yields the following system of differential equation and boundary conditions.

$$\frac{1}{\xi} \cdot \frac{d}{d\xi} \left(\xi \cdot \frac{d\psi}{d\xi} \right) = \lambda^2 \cdot \psi \quad (3.7a)$$

$$\left. \frac{d\psi}{d\xi} \right|_{\xi=0} = 0 \quad @ \quad \xi = 0 \quad (3.7b)$$

$$\left. \psi \right|_{\xi=+1} = \psi_w \quad @ \quad \xi = +1 \quad (3.7c)$$

Equation 3.7a has a mathematical form of a Bessel's differential equation (Kreyszig, 1999). In consequence, there exists an analytical solution for this system and this is given by the following expression.

$$\psi(\xi) = \psi_w \cdot \frac{I_0(\lambda \cdot \xi)}{I_0(\lambda)} \quad (3.8)$$

where I_0 is the modified Bessel function of first kind that is conveniently tabulated or available in computational software.

A system such as the one just described above has been studied and its solution reported in the literature (Masliyah, 1994; Wu and Papadopoulos, 2000). Equation 3.8 is in good agreement with those previous reports.

3.2.3 Capillary System with Annular Geometry

The third system under analysis in this present work and chapter is shown in Figure 3.3. This system may be considered as a double cylindrical capillary system where the inner circular wall is subjected to an electrical potential equal to Ψ_1 and, the outer circular wall is

subjected to an electrical potential equal to Ψ_2 . The coordinate system has been anchored at the center of the capillary to take advantage of the symmetry of the geometry. In dimensionless coordinates, the center of the system is at the location $\xi=0$; the inner wall, at $\xi=b$; and the outer wall; $\xi=+1$. In both cases only the positive domain of the radial coordinate has been used.

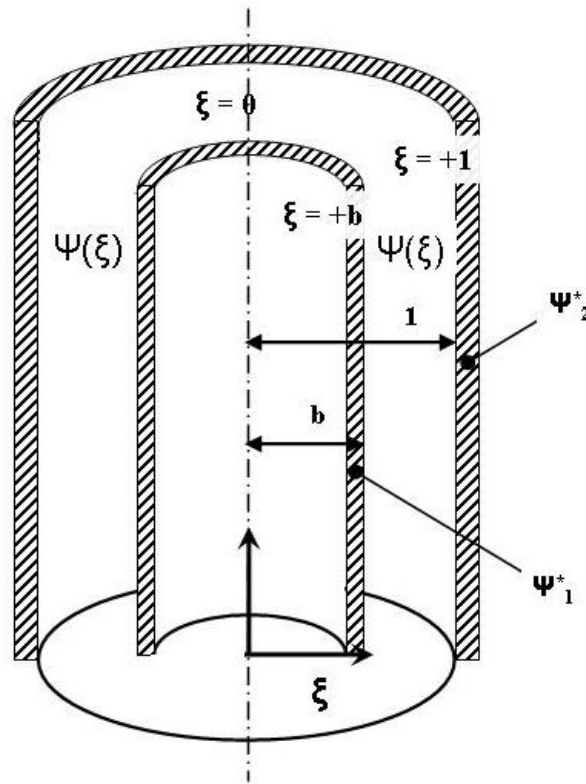


Figure 3.3 Geometrical sketch of an annular capillary channel and coordinate system

As in the two previous cases, the electrostatic potential acting in the system is defined by equation 3.3 and a proper set of boundary conditions. The Debye-Hückel approximation grants a linear differential mathematical expression that for this particular geometry has been identified as the Bessel's differential equation (Kreyszig, 1999). From the analysis, the following expressions model the system described by Figure 3.3 with the corresponding considerations.

$$\frac{1}{\xi} \cdot \frac{d}{d\xi} \left(\xi \cdot \frac{d\psi}{d\xi} \right) = \lambda^2 \cdot \psi \quad (3.9a)$$

$$\psi \Big|_{\xi=b} = \psi_1 \quad @ \quad \xi = b \quad (3.9b)$$

$$\psi \Big|_{\xi=+1} = \psi_2 \quad @ \quad \xi = +1 \quad (3.9c)$$

Although far more complex to be obtained than in the cylindrical case, there exists an analytical solution for annular geometry represented by equation 3.9 a-c. The solution invokes a Bessel approach with evaluation of the respective constants. The final analytical expression is given by

$$\psi(\xi) = \frac{I_0(\lambda \cdot \xi) \cdot [\psi_1 \cdot K_0(\lambda) - \psi_2 \cdot K_0(\lambda \cdot b)] + K_0(\lambda \cdot \xi) \cdot [\psi_2 \cdot I_0(\lambda \cdot b) - \psi_1 \cdot I_0(\lambda)]}{I_0(\lambda \cdot b) \cdot K_0(\lambda) - I_0(\lambda) \cdot K_0(\lambda \cdot b)} \quad (3.10)$$

where I_0 and K_0 are the modified Bessel functions of first and second kind respectively. As indicated before, these functions are conveniently tabulated in the literature or available in efficient computational software.

The analytical expression, equation 3.10, obtained in this work is in good agreement with the analysis of a capillary system with annular geometry reported in the literature (Wu and Papadopoulos, 2000; Kang et. al., 2002). Furthermore, the complexity of the electrostatic expression for the annular case clearly indicates that system geometry plays a significant role in the determination of the electroosmotic flow regime. This early conclusion is encouraging for the continuation of this thesis. However, nothing has been mentioned about the effect of the Debye-Hückel approximation. For this reason, the next section is dedicated to analyze the consequences on electrostatic potential prediction when using analytical expressions such as those of equations 3.6, 3.8 and 3.10.

3.3 The effects of Approximations

System geometry is intrinsic to any fundamental equation, and thus, this feature has been identified as an aspect that may influence hydrodynamic velocity. To introduce the geometrical aspect into play, an analytical expression has been developed using the Debye-Hückel approximation. However, no systematic analysis has been conducted to verify the effect of the most typical approximation when compared with the real solution. This issue is important to the present study in that approximation errors may lead to the wrong conclusions.

Just to remember, the Debye-Hückel approximation claims that the hyperbolic sine of the electrostatic potential is approximately equal to the electrostatic potential ($\sinh \psi \approx \psi$). The main reason for this approximation is obviously the convenient analytical solution of the equation 3.3. However, this simplification obligates the restriction that the applied electrostatic potential cannot be predicted beyond values of 25 mV. In other words, this simplified solution is only valid in the range of $-1 \leq \psi \leq +1$ which is rather small for electrostatic potential values (Masliyah, 1994). In fact, electrostatic applications related to remediation processes report electrostatic potential as high as 100 – 200 mV (Kang, Yang and Huang, 2002). These reported values of electrostatic potential are four an even eight times higher than the restriction specified for the approximation.

To evaluate the real dimension of results when applying the Debye-Hückel approximation, the three electrostatic potential analytical expressions were plotted and compared with the corresponding numerical solution of the complete Poisson-Boltzmann equation. In particular, the comparison is presented in Figures 3.4, 3.5 and 3.6. In all these cases, the continuous lines represent the exact numerical solution. Figure 3.4, for the planar example, shows the electrostatic potential variation, along the transversal coordinate ξ , predicted by the numerical solution of the complete Poisson-Boltzmann equation and the solution given by the Debye-Hückel linear approximation. In particular, Figure 3.4 demonstrates that not only the predictions of the electrostatic potential, Ψ , are restricted by the range $-1 \leq \psi \leq +1$ but also by the range of the inverse Debye length, λ . Predictions out of

bound should be expected for the range of $0.1 \leq \lambda \leq +10$. This range leaves most types of fluids out of the possibility of being studied.

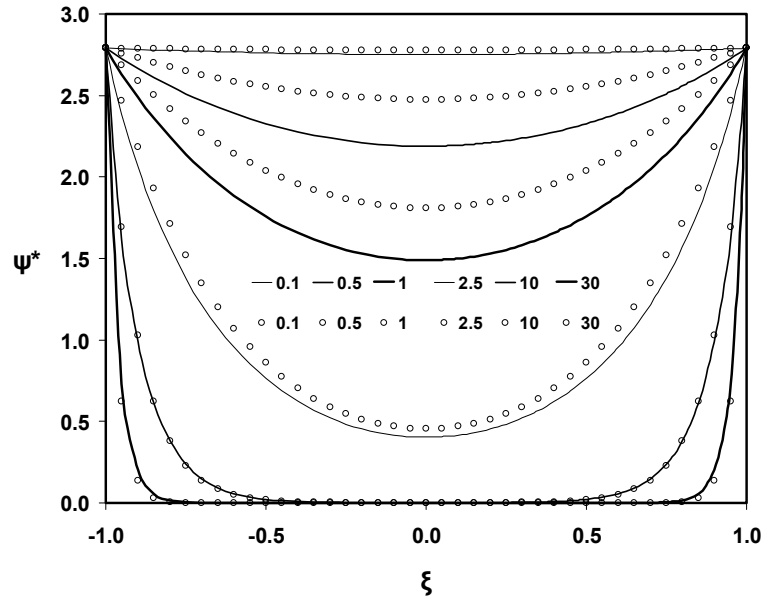


Figure 3.4 Dimensionless electrical potential profiles, in a planar geometry, for various values of the dimensionless inverse Debye length.

For the cylindrical system, figure 3.5 displays values of the electrostatic potential variation, along the radial coordinate ξ , predicted by the numerical solution obtained by the method of Euler of the complete Poisson-Boltzmann equation for this geometry and the solution given by the Debye-Hückel linear approximation. As in the case of the capillary in a rectangular geometry, figure 3.5 demonstrates that predictions of the electrostatic potential, Ψ , for the case of cylindrical geometry, are restricted by the range $-1 \leq \psi \leq +1$ and by the range of the inverse Debye length, λ . Fluids that exhibit an electroosmotic behavior in the domain of the inverse Debye length of $0.1 \leq \lambda \leq +10$ cannot be studied using the analytical expression yielded by the Debye-Hückel approximation.

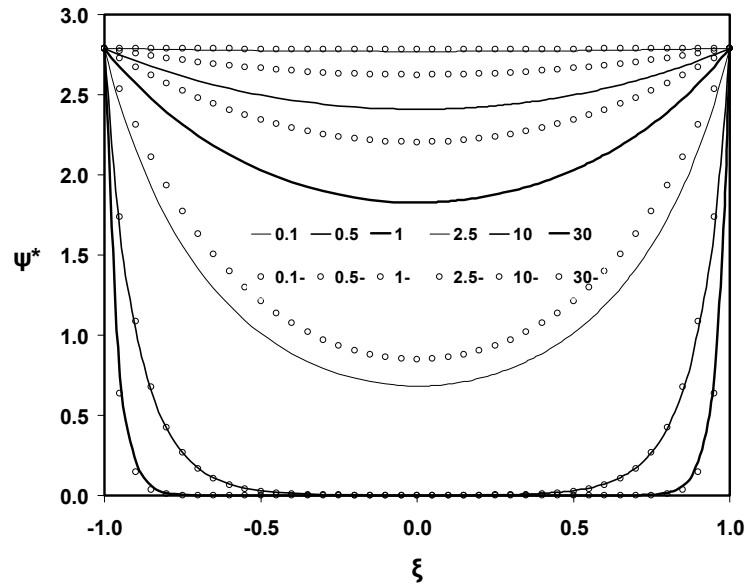


Figure 3.5 Dimensionless electrical potential profiles, in a cylindrical geometry, for various values of the dimensionless inverse Debye length.

The last expression to be evaluated corresponds to that obtained for the annular geometry. Figure 3.6 shows the electrostatic potential variation, along the radial coordinate ξ , predicted by the numerical solution of the complete Poisson-Boltzmann equation and the solution given by the Debye-Hückel linear approximation. Figure 3.6 depicts only the right hand side of the annular section for a radius ratio $b=0.4$ on the inner core. In particular, Figure 3.6 confirms the two previous observations on the effect of prediction using analytical expressions yielded by the Debye-Hückel approximation. In general, figure 3.6 shows that no many fluid types may be studied using this source of analytical expressions. The reason is that not only the predictions of the electrostatic potential, Ψ , are restricted by the range $-1 \leq \psi \leq +1$ but also by the range of the inverse Debye length, λ . Predictions of electrostatic potential for fluids that behave within the range of $0.1 \leq \lambda \leq +10$ are expected to have high deviation from true values.

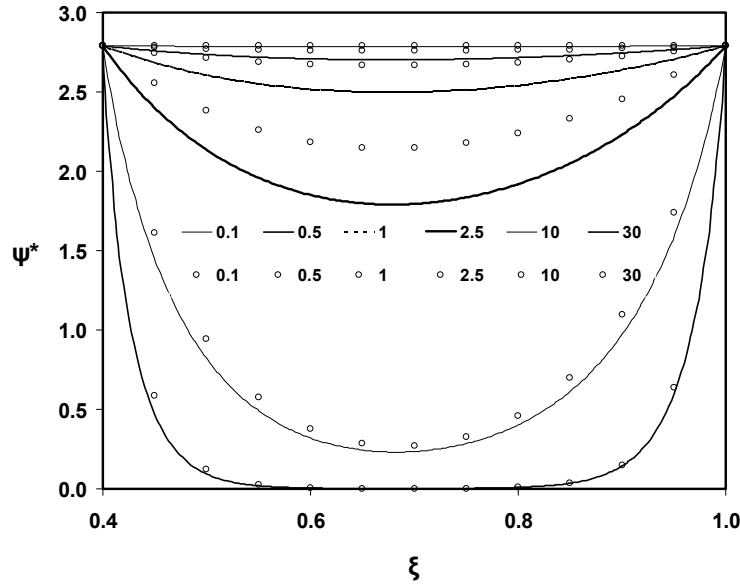


Figure 3.6 Dimensionless electrical potential profiles, in an annular geometry, for various values of the dimensionless inverse Debye length.

The three cases analyzed in this section present consistent disagreement with the numerical solution of the complete original equation, i.e., the Poisson-Boltzmann equation. Considering that the analytical expression have been tested out of the suggested range $-1 \leq \psi \leq +1$ of application, the results do not necessarily invalidate the Debye-Hückel approach. However, the results clearly indicate that more realistic electrostatic potential values cannot be predicted using the analytical expressions yielded by the approximation. If this is true, as proven, the direct implication is that not many electroosmotic studies are valid. In fact, the issue has called the attention of only a few numbers of researchers but with little response and not great results. This simple but important information is the engine of motivation to develop an alternative solution to the complete Poisson-Boltzmann equation. The next chapter is dedicated to finding this new approach leading to a more accurate analytical expression of a non-linear differential equation.

3.4 Summary of the Chapter

Electroosmosis is one of the important driving forces in the transport of solute through porous media when an electrical field is applied. The direct relationship between electroosmosis and electrostatic potential obligates the study of this later one. In this chapter, basic aspects of electrostatics fields that apply to electroremediation are introduced and discussed.

First, the role of the electrostatic potential, in the context of hydrodynamic, is established. Also, the convenience of using analytical expressions in the analysis of the effects of the electrostatic potential on other electrokinetic variables is discussed.

This chapter also introduces the fundamental equations that describe electrostatic potential, i.e., the Poisson and Poisson-Boltzmann equations. The common simplification to the Poisson-Boltzmann equation is presented and applied. Analytical models are developed using three target geometries.

Finally, this chapter analyzes the implication of using the Debye-Hückel approximation. The obtained analytical expressions are used to extrapolate electrostatic potential predictions within practical values. The results are analyzed and further efforts are established.