



A finite difference approach to solve the nonlinear model of electro-osmotic flow in nano-channels

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Abstract

This article considers a system of coupled equations constructed by the nonlinear model of electro-osmotic flow through a one-dimensional nano-channel. Functions that belong to this system include distributions of mole fraction of cation and anion, electrical potential, and velocity. We try to find an accurate closed-form solution. To this end, some mathematical approaches are concurrently used to convert the equations to a nonlinear differential equation in terms of the mole fraction of anion. The latter nonlinear differential equation is transformed into a nonlinear algebraic system by the finite difference method, and the system's solution is obtained using Newton's iterative algorithm. Furthermore, equations for the mole fraction of cation, electrical potential, and velocity in terms of the mole fraction of anion are obtained. We calculate errors by substituting the proposed solution into the equations to validate the results. Comparing the results with some other numerical research works demonstrates an acceptable accuracy.

Keywords. Electro-osmotic flow, Nano-channels, Closed-form solution, Finite difference, Newton iterative algorithm.

1991 Mathematics Subject Classification. 7676, 65Lxx.

1. INTRODUCTION

Novel applications of nanotechnology including, targeted drug delivery, biophysical chemistry, and nanomembrane design have attracted many researchers and industries [18, 20, 21]. In a more general perspective, miniaturization stands out as one of the most rapid advancements in the realm of science and technology over the past century. Around four decades ago, the terms "micro and nanofluidics" emerged with the inception of micro-fabricated fluid systems at institutions like Stanford University (for gas chromatography) and IBM (for inkjet printer nozzles) [10]. Inhomogeneous mixtures, the usual mass transfer balance is between Fickian diffusion and convection [3]; and as an application, this concept is important in the performance determination of an absorption heat pump [4]. Electro-osmosis, is defined as the motion of a fluid due to an externally applied electric field. Electro-osmotic flow is usually present in a micro/ nanochannel or a porous medium where an external electrical field is present. To be a more specific, the flow behavior of a mixture consisting of two monovalent ions plus an aqueous solvent between parallel plates is our interest here. To see the considered mixture detailed explanation refer to references [5, 7–9, 12–14, 19]. In the electro-osmotic flow presented here, the Reynolds number is minimal thus convection is neglected. In addition, asymmetric potential distributions will be taken into consideration. Other physical assumptions governing phenomena and detailed explanations for notations used here (nomenclature) are mentioned in [22]; while some of them are introduced in section 2. Finally, four coupled nonlinear equations are derived for the mole fractions of anion and

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cation, electrical potential, and velocity. We convert the nonlinear system to a nonlinear ordinary differential equation and a finite difference approach is used in a combination of central difference and forward difference for second and first derivatives. Then the discretized system of nonlinear equations is solved by Newton method with a suitable start point which is obtained via interpolating of boundary conditions. Furthermore, the rest primary equations (three of four) can be easily solved.

TABLE 1. Nomenclature.

ϕ^*	Electrical potential	Volt
ϕ	Dimensionless electrical potential	
ϕ_0	Potential scale	RT /F
r^*	Vector of location	nm
ε_r	Dielectric constant	$= 8.854e - 12C/V.m$
ε_0	Permittivity of free space	-
ρ_i	Number density	$Na.c_i(Numbers/m^3)$
Na	Avogadro number	$= 6.022e23$
z_i	Valence of ion	-
c_i	Concentration of ion	$Mole/m^3$
C	Total molar Concentration	$= \sum c_i + c_{solvent}$
X_i	Mole fraction of ion	$= c_i/c$
I	ionic strength	$= \sum z_i c_i^2$
T	Temperature	K
F	Faraday's constant	$= 96485.3415 C/mole$
K	Boltzmann constant	$= 1.38065e - 23 j/k$
R	Universal ideal gas constant	$= 8.3144 j/mole.k$
λ	Debye length	$= \frac{1}{F} \sqrt{\frac{\varepsilon RT}{I}}$
u^*	velocity	$m.s^{-1}$
U_0	average electro-osmotic velocity	$m.s^{-1}$
U	Dimensionless velocity	
μ	Viscosity	$Kg.m^{-1}.s^{-1}$
D_i	Diffusion coefficient	-
Re	Reynolds number	$= \rho U_0 h / \mu$
Sc	Schmidt number	$= \mu / \rho D_i$
x^*, y^*, z^*	Cartesian coordinate	-
x, y, z	Dimensionless Cartesian coordinate	
Subscripts	- , +	

2. MATHEMATICAL MODEL

The fundamental governing equations for three-dimensional electro-osmotic flow consist of the Poisson equation, governing the electric field; the Navier-Stokes equation, governing the flow field; and the mass transfer equation. These equations are typically represented in their general three-dimensional form. Assuming a dilute mixture, the mass transfer equation simplifies to what is known as the Poisson-Nernst-Planck (PNP) equations. (see [1, 2, 11, 19]). In current research, the mathematical problem expression is mainly in accordance to [22] and the mentioned notations. The geometry of one dimensional channel is shown in Figure 1. We get a brief review on Poisson equation and for detailed explanations of Navier-Stokes and mass transfer equations refer to [11, 22].

$$\nabla^2 \phi^*(r^*) = -\frac{1}{\varepsilon_r \varepsilon_0} e \sum_i z_i \rho_i(r^*) = -\frac{1}{\varepsilon_r \varepsilon_0} e n_a \sum_i z_i c_i(r^*) = -\frac{1}{\varepsilon_r \varepsilon_0} F c \sum_i z_i X_i(r^*), \quad (2.1)$$



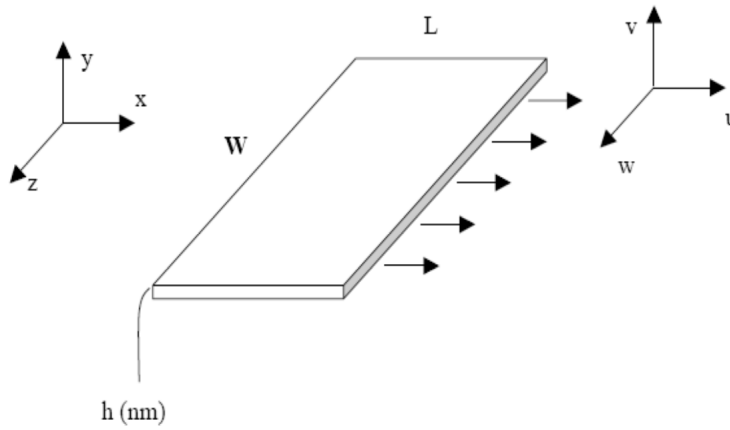


FIGURE 1. One-dimensional channel $w \gg h, L \gg h$.

where the parameters are given in "nomenclature".

Applying non-dimensional variables such as, $\phi(r(x, y, z)) = \frac{\phi^*(r^*)}{\phi_0}$, $x = \frac{x^*}{L}$ and $z = \frac{z^*}{w}$ we can get,

$$\nabla^2 \phi = -\frac{Fch^2}{\epsilon_e \phi_0} \sum_i z_i X_i, \tag{2.2}$$

where $\epsilon_1 = \frac{h}{L}$, $\epsilon_2 = \frac{h}{w}$, $\epsilon_e = \epsilon_r \epsilon_0$ and $\phi_0 = \frac{KT}{e} = \frac{RT}{F}$ (K, T and R are given in nomenclature). If the volume of ions neglected, then we have,

$$\nabla^2 \phi = -\frac{\beta}{\epsilon^2} \sum_i z_i X_i, \tag{2.3}$$

where $\epsilon = \frac{\lambda}{h}$ and $\beta = \frac{c}{I}$ also parameters λ, c and I introduced in nomenclature.

Under the assumption of a dilute mixture, the mass transfer equations simplify to the Poisson-Nernst-Planck equations. Then, considering [22], in the case of a one-dimensional channel the governing equations are in the following form,

$$\frac{d^2 \phi}{dy^2} = -\frac{\beta}{\epsilon^2} \sum_i X_i, \tag{2.4}$$

$$\frac{d^2 X_i}{dy^2} + \frac{d}{dy} \left(X_i, \frac{d\phi}{dy} \right) = 0, \tag{2.5}$$

$$\frac{d^2 u}{dy^2} = -\frac{\beta}{\epsilon^2} \sum_i X_i. \tag{2.6}$$

Comparing Equation (2.4) with Equation (2.6), we find out that dimensionless potential ϕ and dimensionless velocity u are governed by the same differential equations. Whenever the electrolyte consists of monovalent cation and anion



(take sodium chloride as an example), then Equations (2.4)-(2.6) can be written as

$$\frac{d^2\phi}{dy^2} = -\frac{\beta}{\varepsilon^2}(X_+ - X_-), \quad (2.7)$$

$$\frac{d}{dy}\left(\frac{dX_+}{dy} + X_+\frac{d\phi}{dy}\right) = 0, \quad (2.8)$$

$$\frac{d}{dy}\left(\frac{dX_-}{dy} - X_-\frac{d\phi}{dy}\right) = 0, \quad (2.9)$$

$$\frac{d^2u}{dy^2} = -\frac{\beta}{\varepsilon^2}(X_+ - X_-). \quad (2.10)$$

Where X_- and X_+ are mole fractions of anion and cation respectively. Boundary conditions of Equations (2.7)-(2.10) are given in the following form,

$$\begin{cases} \phi(0) = \phi(1) = 0, & X_-(0) = X_-(1) = X_-^0, \\ u(0) = u(1) = 0, & X_+(0) = X_+(1) = X_+^0. \end{cases} \quad (2.11)$$

Of course, the boundary conditions for ϕ and u are not always the same. The above system of differential equations with boundary conditions was solved in [22] but to decrease the computational operations we convert this system to one differential equation in terms of the mole fraction of anion with boundary condition. Then, the rest of the unknown functions can be easily computed.

3. REDUCING TO AN ODE

Equations (2.7) and (2.10) are equivalent and the boundary conditions for those equations are the same, so we only have to solve Equations (2.7)-(2.9). According to (2.8) and (2.9) it is obvious that,

$$\phi(1) - \phi(0) = a \int_0^1 \frac{dy}{X_+} - \ln\left(\frac{X_+(1)}{X_+(0)}\right), \quad \phi(1) - \phi(0) = b \int_0^1 \frac{dy}{X_-} + \ln\left(\frac{X_-(1)}{X_-(0)}\right). \quad (3.1)$$

Replacing boundary condition of (2.11) into Equation (3.1), we obtain $a = b = 0$. For (2.8) and (2.9) we can write,

$$\int_0^y d\phi = -\int_{X_+^0}^{X_+} \frac{dX_+}{X_+} \quad \text{and} \quad \int_0^y d\phi = -\int_{X_-^0}^{X_-} \frac{dX_-}{X_-} \quad \text{then} \quad \phi(y) = -\ln\left(\frac{X_+}{X_+^0}\right), \quad \phi(y) = \ln\left(\frac{X_-}{X_-^0}\right). \quad (3.2)$$

Since $\ln\left(\frac{X_-}{X_-^0}\right) = -\ln\left(\frac{X_+}{X_+^0}\right)$, we have

$$X_+(y) \cdot X_-(y) = X_+^0 \cdot X_-^0. \quad (3.3)$$

Differentiating (3.2) respect to y , substituting the results into (2.7) and using (3.3), we find a nonlinear differential equation with boundary condition in this form,

$$\begin{cases} X_- \frac{d^2X_-}{dy^2} - \left(\frac{dX_-}{dy}\right)^2 + \frac{X_+^0 X_-^0 \beta}{\varepsilon^2} X_- - \frac{\beta}{\varepsilon^2} X_-^3 = 0, \\ X_-(0) = X_-(1) = X_-^0, \end{cases} \quad (3.4)$$

where values of Equation (3.4) are given in [22],

$$\begin{aligned} \varepsilon &= 0.04, \quad \beta = 188.679, \\ X_-(0) &= X_-(1) = X_-^0 = 0.00254, \\ X_+(0) &= X_+(1) = X_+^0 = 0.00276. \end{aligned} \quad (3.5)$$

To solve nonlinear differential equations there are some computational techniques such as, new homotopy perturbation method [16], modified homotopy perturbation with the help of Fourier transform and homotopy perturbation method [6, 17]. But to solve nonlinear differential Equation (3.4) we use a combination of finite difference and Newton iterative algorithm methods. The start point in the algorithm is found using an interpolation of boundary conditions (3.4).



4. FINITE DIFFERENCE AND NEWTON ITERATIVE ALGORITHM

To solve differential equation with boundary condition (3.4) we use a combination of central difference and forward difference for second and first derivatives in (3.4). It would be discretized to an algebraic nonlinear system as follows,

$$\begin{cases} X_-(y_i) \left(\frac{X_-(y_{i+1}) - 2X_-(y_i) + X_-(y_{i-1}))}{h^2} \right) - \left(\frac{X_-(y_{i+1}) - X_-(y_{i-1}))}{2h} \right)^2 + \frac{X_+^0 X_-^0 \beta}{\varepsilon^2} X_-(y_i) - \frac{\beta}{\varepsilon^2} (X_-(y_i))^3 = 0, \\ i = 1, 2, \dots, n-1, h = \frac{y_n - y_0}{n}. \end{cases} \quad (4.1)$$

In other words we can write,

$$\begin{aligned} g_1(X_-(y_1), \dots, X_-(y_{n-1})) &= X_-^2(y_2) + 8X_-^2(y_1) + X_-^2(y_0) - 4X_-(y_1)X_-(y_0) - 4X_-(y_1)X_-(y_2) \\ &\quad - 2X_-(y_2)X_-(y_0) - 4h^2\eta X_-(y_1) + 4h^2\lambda X_-^3(y_1) = 0, \\ g_2(X_-(y_1), \dots, X_-(y_{n-1})) &= X_-^2(y_3) + 8X_-^2(y_2) + X_-^2(y_1) - 4X_-(y_2)X_-(y_1) - 4X_-(y_2)X_-(y_3) \\ &\quad - 2X_-(y_3)X_-(y_1) - 4h^2\eta X_-(y_2) + 4h^2\lambda X_-^3(y_2) = 0, \\ &\vdots \\ g_n(X_-(y_1), \dots, X_-(y_{n-1})) &= X_-^2(y_n) + 8X_-^2(y_{n-1}) + X_-^2(y_{n-2}) - 4X_-(y_{n-1})X_-(y_{n-2}) - 4X_-(y_{n-1})X_-(y_n) \\ &\quad - 2X_-(y_n)X_-(y_{n-2}) - 4h^2\eta X_-(y_{n-1}) + 4h^2\lambda X_-^3(y_{n-1}) = 0, \\ y_j &= \frac{j}{n}, j = 0, 1, \dots, n, \\ X_-(0) &= X_-(1) = 0.00254. \end{aligned} \quad (4.2)$$

We show nonlinear algebraic system (4.2) by $G((g_1, g_2, \dots, g_n)^T) = \vec{0}$ and it could be converted to a linear tridiagonal algebraic system with the help of Newton iterative algorithm; where interpolation of boundary conditions is utilized to determine the start point of the algorithm. Thus

$$\begin{aligned} X_-^{(0)} &= (0.00254, 0.00254, \dots, 0.00254)^T, \\ X_-^{(k)} &= (X_-(y_0), \dots, X_-(y_{n-1}))^T, \\ J(X_-^{(k)}) (X_-^{(k+1)} - X_-^{(k)}) &= -G(X_-^{(k)}), k = 1, 2, \dots, m, \end{aligned} \quad (4.3)$$

where m is the iteration number and Jacobian matrix is defined in this form,

$$J(H_-^{(k)}) = \begin{bmatrix} \frac{\partial g_1}{\partial X_-(y_1)} & \frac{\partial g_1}{\partial X_-(y_2)} & \cdots & \frac{\partial g_1}{\partial X_-(y_{n-1})} \\ \frac{\partial g_2}{\partial X_-(y_1)} & \frac{\partial g_2}{\partial X_-(y_2)} & \cdots & \frac{\partial g_2}{\partial X_-(y_{n-1})} \\ \vdots & \vdots & \ddots & \vdots \\ \frac{\partial g_n}{\partial X_-(y_1)} & \frac{\partial g_n}{\partial X_-(y_2)} & \cdots & \frac{\partial g_n}{\partial X_-(y_{n-1})} \end{bmatrix} \quad (4.4)$$

Assuming $X_-^{(0)}$ as a start point and $H_-^{(k)} = H_-^{(k+1)} - X_-^{(k)}$ in (4.3), we compute $H_-^{(k)}$ and $H_-^{(k+1)}$ for $k = 1, 2, \dots, m$. The values in 7 nodes with $k = 3$ (iterations) are computed. The following polynomial is given by interpolation,

$$\begin{aligned} X_-(y) &= 0.00254 + 0.00187164y - 0.01437371y^2 + 0.06277625y^3 - 0.16908649y^4 \\ &\quad + 0.28638872y^5 - 0.29738070y^6 + 0.17307239y^7 - 0.0432681y^8. \end{aligned} \quad (4.5)$$

(4.5) is a closed-form of solution for mole fraction of anion distribution which can be helpful for future studies in this research area. Now, we can evaluate error of the presented method by substituting the above closed-form of solution in equation of mole fraction of anion distribution (3.4). The corresponding results are given in Table 2.

By substituting (4.5) into (3.3) and applying values of boundary conditions (3.5), we obtain a closed-form of solution for equation of mole fraction of cation distribution in the following form,

$$\begin{aligned} X_+(y) &= 0.0000070104(0.00254 + 0.00187164y - 0.01437371y^2 + 0.06277625y^3 - 0.16908649y^4 \\ &\quad + 0.28638872y^5 - 0.29738070y^6 + 0.17307239y^7 - 0.043268099y^8)^{-1}. \end{aligned} \quad (4.6)$$



TABLE 2. Absolute error for the closed-form solution (4.5).

y	Absolute error
0	9.0×10^{-5}
0.1	8.8×10^{-6}
0.2	9.4×10^{-7}
0.3	3.7×10^{-7}
0.4	2.7×10^{-8}
0.5	2.6×10^{-8}
0.6	2.7×10^{-8}
0.7	3.7×10^{-7}
0.8	9.4×10^{-7}
0.9	8.8×10^{-6}
1.0	9.0×10^{-5}

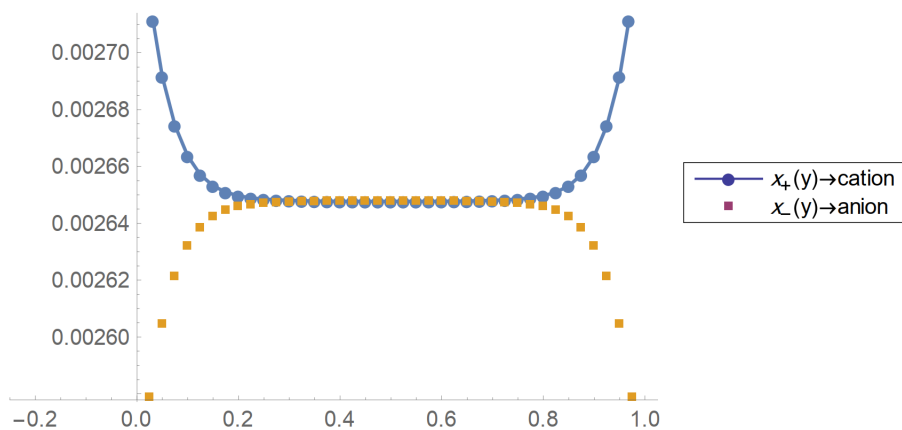


FIGURE 2. Curves of solutions for anion and cation.

TABLE 3. The cation and anion distribution values.

y	$X_+(y)$	$X_-(y)$
0	0.00276	0.00254
0.1	0.00266365	0.00263188
0.2	0.00264967	0.00264577
0.3	0.00264807	0.00264736
0.4	0.00264775	0.00264768
0.5	0.00264773	0.00264770
0.6	0.00264775	0.00264768
0.7	0.00264807	0.00264736
0.8	0.00264967	0.00264577
0.9	0.00266365	0.00263188
1.0	0.00276	0.002548

We consider the proposed solutions for mole fraction of cation and anion distribution by Figure 2.

The values of sodium mole fraction $X_+(y)$ and chloride mole fraction $X_-(y)$ according to (4.5) and (4.6) are given by the Table 3.



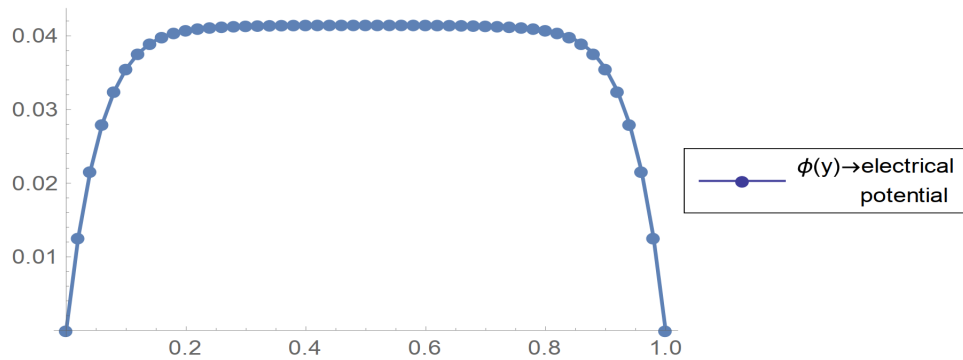


FIGURE 3. Curve of solution for electrical potential.

TABLE 4. Absolute errors.

y	[15]	proposed method
0	7.2×10^{-6}	9.0×10^{-5}
0.1	1.5×10^{-7}	8.8×10^{-6}
0.2	5.1×10^{-6}	9.4×10^{-7}
0.3	1.6×10^{-6}	3.7×10^{-7}
0.4	1.6×10^{-6}	2.7×10^{-8}
0.5	1.6×10^{-6}	2.6×10^{-8}
0.6	1.6×10^{-6}	2.7×10^{-8}
0.7	1.6×10^{-6}	3.7×10^{-7}
0.8	1.5×10^{-6}	9.4×10^{-7}
0.9	5.1×10^{-7}	8.8×10^{-6}
1.0	7.2×10^{-6}	9.0×10^{-5}

The wall mole fractions are constants, for sodium the wall mole fraction is 0.00276 (curve of cation); for chloride, the wall mole fraction is 0.00254 (curve of anion). Difference of $X_-(y)$ and $X_+(y)$ for $y = 0.5$ is equal to 3×10^{-8} (This value seem more accurate than what the authors in [22] gave).

Also, with the help of (3.2) and closed-form of solution for mole fraction of anion distribution (4.5), we can give solution of electrical potential and velocity to this form,

$$\phi(y) = \ln\left(\frac{X_-}{X_-^0}\right) = \ln(1 + 0.73686702y - 5.65894251y^2 + 24.71505941y^3 - 66.56948574y^4 \tag{4.7}$$

$$+ 112.75146496y^5 - 117.07901787y^6 + 68.13873961y^7 - 17.03468490y^8). \tag{4.8}$$

Since Equations (2.7) and (2.10) are equal, then $\phi(x) = u(y)$. Therefore, we show solution of electrical potential by Figure 3.

5. COMPARISON AND DISCUSSIONS

The coupled nonlinear system (2.7)-(2.10) is solved in [22]. However, we reformulate this system into a nonlinear differential equation, which not only reduces computational complexity compared to [22] but also increases accuracy. In [15], the problem is addressed using the homotopy perturbation method, yielding a solution with good accuracy. A comparison of our results with those in [15] for the solution of the mole fraction of anion distribution (4.5) is presented in Table 4. As demonstrated, the proposed method achieves high accuracy.



CONCLUSION

In this research, we applied a method to solve a nonlinear differential equation with boundary conditions that governs the flow in Nano-channels. A polynomial is introduced as the closed-form solution that could be used for any analysis. According to the closed-form solution, some graphs and numerical results illustrate ions mole fraction, electric potential, and velocity. Comparing our results with previous applied methods, it is concluded that the proposed method could be considered a simple way to solve identical nonlinear problems.

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