This paper aims to examine the electro-kinetic flow through nano-channels. The equations governing the fluid flow in a one dimensional channel are derived from the Poisson-Nernst-Planck theory. The boundary conditions for the governing equations are obtained from the electrochemical equilibrium requirements. The coupled equations are transformed into a single differential equation. The transformed equation is solved by He’s homotopy perturbation method and an exact solution is achieved. The validity of results is verified by comparing with existing numerical results. The results are presented for velocity profiles, electrical potential distributions, mole fraction of cation and anion distributions and other physical properties. The results demonstrate reasonable agreement with those provided by other numerical methods and good accuracy of the obtained analytical solutions.

**Key words:** electro-kinetic flow, nano-channels, homotopy perturbation method (HPM)

**Nomenclature**

- $\phi^*$ – electrical potential [V]
- $\phi$ – dimensionless electrical potential [-]
- $\phi_0$ – potential scale, $\phi = RT/F$
- $r^*$ – vector of location [nm]
- $\varepsilon_r$ – dielectric constant, $\varepsilon_r = 8.854 \cdot 10^{-12}$ C/(Vm)
- $\varepsilon_0$ – permittivity of free space [-]
- $\rho_i$ – number density, $\rho_i = N_A c_i$ [number/m$^3$]
- $N_A$ – Avogadro number, $N_A = 6.022 \cdot 10^{23}$
- $z_i$ – valence of ion [-]
- $c_i$ – concentration of ion [mole/m$^3$]
- $c$ – total concentration, $c = \sum c_i + c_{solvent}$
- $X_i$ – mole fraction of ion, $X_i = c_i/c$
- $I$ – ionic strength, $I = \sum z_i c_i^2$
- $T$ – temperature [K]
- $F$ – Faraday constant, $F = 96485.3415$ C/mole
- $k$ – Boltzmann constant $k = 1.38065 \cdot 10^{23}$ j/k
- $R$ – universal ideal gas constant, $R = 8.3144$ j/(mole.k)
- $\lambda$ – Debye length, $\lambda = F^{-1} \sqrt{\varepsilon_{r} F R T T'}$
- $u^*$ – velocity [m/s]
- $u_0$ – average electro-osmotic velocity [m/s]
- $u$ – dimensionless velocity
- $\mu$ – viscosity [Kg/(ms)]
- $D_i$ – Diffusion coefficient [-]
1. Introduction

Miniaturization has been one of the swiftest revolutions in the scientific and industrial world during last century. The term “micro and nano fluidics” was invented about 40 years ago when micro-fabricated fluid systems were developed at Stanford (gas chromatography) and at IBM (ink jet printer nozzles) (Zheng, 2003). Micro and nano fluidics, the study of fluid flow in micrometer or nanometer sized devices, is one of the disciplines on which the operation of MEMS-NEMS depends. In recent years, scientists have studied the transport of fluids through micro and nano channels, analyzed aqueous solutions with a number of electrolytes, and calculated electric fields, flow fields and ion distributions. The derived differential equations are strongly nonlinear and coupled. Results of solving those nonlinear equations can help scientists to deeply know the described process. The solutions of these nonlinear equations are normally obtained by using, for example, traditional finite difference methods. In numerical methods, stability and convergence should be considered to avoid divergence or inappropriate results. It is often so hard to gain an analytical solution for these kinds of problems which include nonlinear terms. In recent decades, analytical solutions have developed for nonlinear differential equations. One of these methods is the Homotopy Perturbation Method (HPM).

The homotopy perturbation method was introduced by Ji-Huan He for the first time (1999, 2000a,b, 2001, 2003, 2006, 2009). This method has been used by many authors such as Ganji and Sadighi (2006,2007), Ganji et al. (2007a,b) and the corresponding ones included in authors’ references (Ariel et al., 2006; Ariel, 2010; Biazar and Ghazvini, 2007; Ghorbani and Saber-Nadjafi, 2007; Gorji, et al., 2007; Tari et al., 2007; Yusufoglu, 2007). These papers are published to handle a wide variety of scientific and engineering applications such as linear and nonlinear, homogeneous and inhomogeneous as well, because this method continuously transforms a difficult problem into a simplest form, which is solvable. It has been shown by many authors that these methods provide improvements over existing numerical techniques. These methods give successive approximations of high accuracy of solutions.

The aim of this paper is to analytically study the electro-kinetic flow in a nano-channel. The results are compared with numerical outcomes presented in pervious works. However, an analytical expression is more convenient for engineering calculations and is also the obvious starting point for a better understanding.

2. Homotopy perturbation method

To explain this method, let us consider the following function

\[ A(u) - f(r) = 0 \quad r \in \Omega \]  

(2.1)

with the boundary conditions

\[ B(u, \frac{\partial u}{\partial n}) = 0 \quad r \in \Gamma \]  

(2.2)

where \( A, B, f(r) \) and \( \Gamma \) are a general differential operator, a boundary operator, a known analytical function and the boundary of the domain \( \Omega \), respectively.
Generally speaking, the operator $A$ can be divided into a linear part $L$ and a nonlinear part $N(u)$. Equation (2.1) can therefore be written as

$$L(u) + N(u) - f(r) = 0$$

(2.3)

By the homotopy technique, we construct a homotopy $u(r,p) : \Omega \times [0,1] \rightarrow R$. This satisfies

$$H(v,p) = (1-p)[L(v) - L(u_0)] + p[A(v) - f(r)] = 0 \quad p \in [0,1] \quad r \in \Omega$$

(2.4)

or

$$H(v,p) = L(v) - L(u_0) + pL(u_0) + p[N(v) - f(r)] = 0$$

(2.5)

where $p \in [0,1]$ is an embedding parameter, while $u_0$ is the initial approximation of Eq. (2.1), which satisfies the boundary conditions. Obviously, from Eqs. (2.4) and (2.5) we will have

$$H(v,0) = L(v) - L(u_0) = 0 \quad H(v,1) = A(v) - f(r) = 0$$

(2.6)

The changing process of $p$ from zero to unity is just that of $v(r,p)$ from $u_0$ to $u(r)$. In topology, this is called deformation, while $L(v) - L(u_0)$ and $A(v) - f(r)$ are called homotopy.

According to the HPM, we can first use the embedding parameter $p$ as a “small parameter”, and assume that the solutions to Eqs. (2.4), (2.5) can be written as a power series in $p$

$$v = v_0 + pv_1 + p^2v_2 + \ldots$$

(2.7)

Setting $p = 1$ yields in the approximate solution to Eq. (2.4)

$$u = \lim_{p \to 1} v = v_0 + v_1 + v_2 + \ldots$$

(2.8)

The combination of the perturbation method and the homotopy method is called the HPM, which eliminates the drawbacks of traditional perturbation methods while keeping all its advantage.

Series (2.8) is convergent for most cases. However, the rate of convergence depends on the nonlinear operator $A(v)$. Moreover, He (1999) made the following suggestions:

- The second derivative of $N(v)$ with respect to $v$ must be small because the parameter may be relatively large, i.e. $p \to 1$.
- The norm of $L^{-1}(\partial N/\partial V)$ must be smaller than one so that the series converges.

### 3. Mathematical model

Water is an efficient solvent for most polar molecules and electrolytes, although it does not dissolve many organic substances. Many experiments discussed in this work are done using aqueous solution; however, the model is also effective for other solvents. It is also assumed that the solution in nano-channels is incompressible, which is generally accepted because of the properties of liquids. Furthermore, the electro-osmotic flow in nano-channels is a laminar flow, because the Reynolds number (Re) in this case will be very small. According to Poisson’s equation

$$\nabla^2 \phi^*(r^*) = -\frac{1}{\varepsilon_r \varepsilon_0} \rho_E(r^*) = -\frac{1}{\varepsilon_r \varepsilon_0} e \sum_i z_i \rho_i(r^*)$$

(3.1)
The potential scales $\phi_0$ and $\varepsilon_e$ were defined as
\[
\phi_0 = \frac{KT}{e} = \frac{RT}{F} \quad \varepsilon_e = \varepsilon_0 \varepsilon_r
\] (3.2)
The dimensionless form of governing equations can be gained by applying the following parameters
\[
\phi = \frac{\phi^*}{\phi_0} \quad x = \frac{x^*}{L} \quad y = \frac{y^*}{h} \quad z = \frac{z^*}{W}
\] (3.3)
Subsequently, we have
\[
\varepsilon_2^\alpha \frac{\partial^2 \phi}{\partial x^2} + \frac{\partial^2 \phi}{\partial y^2} + \varepsilon_2^\beta \frac{\partial^2 \phi}{\partial z^2} = -\frac{FCh^2}{\varepsilon_e \phi_0} \sum_i z_i X_i = -\frac{\beta}{\varepsilon_2^\gamma} \sum_i z_i X_i
\] (3.4)
where
\[
\varepsilon_1 = \frac{H}{L} \quad \varepsilon_2 = \frac{h}{W} \quad \varepsilon = \frac{\lambda}{h} \quad \beta = \frac{c}{L} \quad \lambda = \frac{1}{F} \sqrt{\varepsilon_e RT}
\]
For the steady state, the mass transport and momentum equations in the dimensionless form for an electro-chemical system are obtained as follows
\[
\nabla^2 X_i + z_i \nabla \cdot (X_i \nabla \phi) - \text{ReSc} \nabla \cdot (X_i u) = 0
\]
\[
\text{Re} (v \cdot \nabla) v = -\nabla P - \frac{F \phi_0 h z_i X_i}{\mu u_0} \nabla \phi + \nabla^2 v
\] (3.5)
For a one-dimensional channel demonstrated in Fig. 1
\[
\varepsilon_1 = \frac{H}{L} \ll 1 \quad \varepsilon_2 = \frac{h}{W} \ll 1 \quad \text{Re} \ll 1
\]
Therefore, the derivatives respected to the $x$ and $z$ directions were neglected so Eqs. (3.4) and (3.5) reduce to
\[
\frac{d^2 \phi}{dy^2} = -\frac{\beta}{\varepsilon_2^\gamma} \sum_i X_i \quad \frac{d^2 X_i}{dy^2} + z_i \frac{d}{dy} \left( X_i \frac{d \phi}{dy} \right) = 0 \quad \frac{d^2 U}{dy^2} = -\frac{\beta}{\varepsilon_2^\gamma} \sum_i X_i
\] (3.6)
In the nano-channel illustrated in Fig. 1, if the electrolyte consists of monovalent cation and monovalent anion, such as sodium chloride, governing Eqs. (3.6) are gained as follows
\[
\frac{d^2 \phi}{dy^2} = -\frac{\beta}{\varepsilon_2^\gamma} (X_+ - X_-) \quad \frac{d^2 u}{dy^2} = -\frac{\beta}{\varepsilon_2^\gamma} (X_+ - X_-)
\]
\[
\frac{d}{dy} \left( \frac{dX_+}{dy} + X_+ \frac{d \phi}{dy} \right) = 0 \quad \frac{d}{dy} \left( \frac{dX_-}{dy} - X_- \frac{d \phi}{dy} \right) = 0
\] (3.7)
The boundary conditions for described equations, Eqs. (3.7) are
\[
\phi(0) = \phi(1) = 0 \quad u(0) = u(1) = 0 \quad X_- (0) = X_- (1) = X_0^- \quad X_+ (0) = X_+ (1) = X_0^+
\] (3.8)
4. Equation reduction

Equations (3.7)\textsubscript{1,2} are similar in the expression and boundary conditions. Therefore, we only consider Eqs. (3.7)\textsubscript{1} to (3.7)\textsubscript{4} for solution. From Eqs. (3.6)\textsubscript{3} and (3.7)\textsubscript{1} we have

\[
\frac{dX_+}{dy} + X_+ \frac{d\phi}{dy} = a \implies \int_0^1 \frac{d\phi}{dy} dy = \int_0^1 \frac{1}{X_+(a - \frac{dX_+}{dy})} dy \\
\implies \phi(1) - \phi(0) = a \int_0^1 \frac{dy}{X_+} - \ln \frac{X_+(1)}{X_+(0)}
\]

\[
\frac{dX_-}{dy} - X_- \frac{d\phi}{dy} = b \implies \int_0^1 \frac{d\phi}{dy} dy = \int_0^1 \frac{1}{X_-(-b + \frac{dX_-}{dy})} dy \\
\implies \phi(1) - \phi(0) = -b \int_0^1 \frac{dy}{X_-} + \ln \frac{X_-(1)}{X_-(0)}
\]

With combining boundary conditions (3.8)\textsubscript{1,2} with the equations above, we have

\[
a \int_0^1 \frac{dy}{X_+} = 0 \implies A = 0 \quad b \int_0^1 \frac{dy}{X_-} = 0 \implies b = 0
\]

So Eqs. (3.6)\textsubscript{3} and (3.7)\textsubscript{1} could be rewritten in the following forms

\[
\frac{dX_+}{dy} + \int_0^y d\phi = - \int_0^{X_+} \frac{dX_+}{X_+} \implies \phi(y) = - \ln \frac{X_+(1)}{X_+(0)}
\]

\[
\frac{dX_-}{dy} - \int_0^y d\phi = \int_0^{X_-} \frac{dX_-}{X_-} \implies \phi(y) = \ln \frac{X_-(1)}{X_-(0)}
\]

\[
\ln \frac{X_-}{X_+} = - \ln \frac{X_+}{X_+} \implies X_+(y)X_-(y) = X_+^0X_+^0
\]

Finally, substitute Eqs. (4.3) into (3.7)\textsubscript{1}, which leads to

\[
X_+ \frac{d^2X_-}{dy^2} - \left( \frac{dX_-}{dy} \right)^2 + \frac{X_+^0X_+^0}{\varepsilon^2} \frac{\beta}{X_-} - \beta \frac{\varepsilon^2}{X_-^3} = 0
\]

The above ordinary differential equation governs the mole fraction of onion distribution. We applied the HPM on Eq. (4.4) to achieve an analytical solution.

5. Application of homotopy perturbation method

We consider Eq. (4.4) with a monovalent electrolyte such as NaCl, and \( T = 25^\circ C, \ h = 20 \text{ nm}, \ X_+^0 = 0.00276, \ X_-^0 = 0.00254 \), therefore: \( \lambda = 0.86 \text{ nm}, \ \varepsilon = \lambda/h = 0.04, \ I = 294.68 \text{ mole/m}^3, \ \beta = 188.679 \).

According to the HPM, we can construct homotopy of Eq. (4.4) as follows

\[
H(u, P) = (1 - p) \left[ \left( X_-(y) \frac{d^2X_-(y)}{dy^2} - \frac{\beta}{\varepsilon^2} X_-(y) \right)^3 - \left( X_-^0(y) \frac{d^2X_-^0(y)}{dy^2} - \frac{\beta}{\varepsilon^2} X_-^0(y) \right)^3 \right] + p \left[ \left( X_-(y) \frac{d^2X_-(y)}{dy^2} - \frac{\beta}{\varepsilon^2} X_-(y) \right)^3 + \frac{X_+^0X_+^0}{\varepsilon^2} \frac{\beta}{X_-} - \left( \frac{dX_-(y)}{dy} \right)^2 \right] = 0
\]
Substituting $X_0 = X_0 + PX_{-1} + P^2X_{02} + \ldots$ into Eq. (5.1) and rearranging the resultant equation based on powers of $P$-terms, we have

$$P^0:\ \left[(X_0(y)\frac{d^2X_0(y)}{dy^2} - \frac{\beta}{\varepsilon^2}X_0(y) - \frac{X_0(y)\frac{d^2X_0(y)}{dy^2} - \beta}{\varepsilon^2}X_0(y)^3\right] = 0 \quad (5.2)$$

$$X_0(0) = X_0(1) = X^0 = 0.00254$$

$$P^1:\ X_0(y)\frac{d^2X_1(y)}{dy^2} - 3.53773125 \cdot 10^5X_0(y)^2X_1(y) + \frac{d^2X_0(y)}{dy^2}X_1(y)$$

$$- \left(\frac{dX_0(y)}{dy}\right)^2 + \frac{d^2X_0(y)}{dy^2}X_0(y) + 0.8266498688X_0(y) - 1.179243750 \cdot 10^5X_0(y)^3 = 0 \quad (5.3)$$

$$X_1(0) = X_1(1) = 0.0$$

$$P^2:\ \frac{d^2X_2(y)}{dy^2}X_0(y) + \frac{d^2X_1(y)}{dy^2}X_1(y) + \frac{d^2X_0(y)}{dy^2}X_2(y)$$

$$- 2\frac{dX_0(y)}{dy}\frac{dX_1(y)}{dy} - 3.537731250 \cdot 10^5X_0(y)^2X_2(y)$$

$$- 3.537731250 \cdot 10^5X_0(y)X_1(y)^2 + 0.8266498688X_1(y) = 0 \quad (5.4)$$

$$X_2(0) = X_2(1) = 0.0$$

$$P^3:\ \frac{d^2X_3(y)}{dy^2}X_0(y) + \frac{d^2X_2(y)}{dy^2}X_1(y) + \frac{d^2X_1(y)}{dy^2}X_2(y) + \frac{d^2X_0(y)}{dy^2}X_3(y)$$

$$- 2\frac{dX_0(y)}{dy}\frac{dX_2(y)}{dy} - \left(\frac{dX_1(y)}{dy}\right)^2 - 3.537731250 \cdot 10^5X_0(y)^2X_3(y)$$

$$- 7.07546250 \cdot 10^5X_0(y)X_1(y)X_2(y) + 0.8266498688X_2(y)$$

$$- 1.17924375 \cdot 10^5X_1(y)^3 = 0 \quad (5.5)$$

$$X_3(0) = X_3(1) = 0.0$$

$X_n(y)$ can be written as follows by solving Eqs (5.2) to (5.5)

$$X_0 = 0.00254$$

$$X_1(y) = -7.021198794 \cdot 10^{-18}e^{29.97638633Y} - 0.00007328084019e^{29.97638633Y} + 0.00007328084019 \quad (5.6)$$

$$X_2(y) = -2.340399598 \cdot 10^{-18}e^{29.97638633Y} - 0.00002442694673e^{29.97638633Y} + 0.00002442694673$$

$$X_3(y) = -7.106629101 \cdot 10^{-19}e^{29.97638633Y} - 0.00007417248346e^{29.97638633Y} + 0.00007417248346$$

In the same manner, the rest of components was found using the Maple package.

According to the HPM, we can conclude that

$$X_n(y) = \lim_{P \to 1} X_n(y) = X_{-0}(y) + X_{-1}(y) + X_{-2}(y) + \ldots \quad (5.7)$$

Therefore, substituting the values of $X_{-0}(y), X_{-1}(y), X_{-2}(y)$ etc. from Eqs. (5.6) into Eq. (5.7), yields

$$X_n(y) = -1.026419033 \cdot 10^{-17}e^{29.97638633Y} - 0.0001071282146e^{29.97638633Y} + 0.002647128214 \quad (5.8)$$
Substituting Eq. (5.8) into Eqs. (4.3)\_1,2, we found

\[
X_+(y) = 7.01 \cdot 10^{-6}\left(-1.026419033 \cdot 10^{-17}e^{29.97638633Y} - 0.0001071282146e^{-29.97638633Y}
+ 0.002647128214\right)^{-1}
\]

\[
\phi(y) = u(y) = \ln\left[\left(-1.026419033 \cdot 10^{-17}e^{29.97638633Y} - 0.0001071282146e^{-29.97638633Y}
+ 0.002647128214\right)0.00254\right]
\]

The shear stress is provided by derivation of Eq. (5.9)\_2

\[
\tau(y) = \frac{-1.211351711 \cdot 10^{-13}e^{29.97638633Y} + 1.264297932e^{-29.97638633Y}
- 4.041019814 \cdot 10^{-15}e^{29.97638633Y} - 0.0421764244e^{-29.97638633Y} + 1.042176462}{
-4.041019814 \cdot 10^{-15}e^{29.97638633Y} - 0.0421764244e^{-29.97638633Y} + 1.042176462}
\]

6. Results and discussion

The procedure adopted in this paper for the current investigation of the electro-dynamic problem in a nano-channel can be described as follows:

By using some mathematical calculations, the coupled differential equations, Eqs. (3.7), are reduced to Eq. (4.4). Equation (4.4) with the boundary conditions, Eq. (3.8)\_3, is solved by using the HPM. The detailed procedural steps are follows:

- Firstly, the anion mole fraction distribution is computed by solving Eq. (4.4) given with the boundary conditions, Eq. (3.8)\_3.
- Secondly, the electric potential, the velocity and the cation mole fraction distribution are solved by using equations (4.3)\_2 and (4.3)\_3, respectively.

The shear stress is solved by derivation of velocity distribution. In this work, we found that the product of anion mole fraction into cation mole fraction at any point is constant. The comparisons are shown in Figs. 2 and 3 and Table 1, are in very good agreement with the solutions presented by Zheng (2003).

Fig. 2. The comparison between the FDM by Zheng (2003) and HPM solutions for $X_-(y)$ (a) and for $X_+(y)$ (b)
Fig. 3. The comparison between the FDM by Zheng (2003) and HPM solutions for $\phi(y)$ and $u(y)$ (a) and for $\tau(y)$ (b)

Table 1. The comparison between the FDM by Zheng (2003) and HPM solutions

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7. Conclusion

In this paper, we successfully applied the homotopy perturbation method to solve a nonlinear differential equation with given boundary conditions for a nano-channel and showed graphical results of velocity, electric potential and ion mole fraction. The results were compared with the numerical solution available in the literature using the FDM, and a very good agreement was observed. The outcomes prove the effectiveness and accuracy of the HPM. The current work presents a new application of the HPM which could be used for similar problems in a wide range of engineering situations. The key-factor of this paper is based on analytical solution of electro-kinetic problems in a nano-channel. Although these results obviously show that the product of anion mole fraction into cation mole fraction at any point is constant and also in the bulk of the channel, the mole fractions of cations and anions are the same, which implies that the electrolytic solution is neutral in the bulk, and the concentration difference between cation and anion species reaches its maximum at the wall.

References


Analityczne rozwiązania uzyskane perturbacyjną metodą homotopii He’go dla elektrokinetycznego przepływu przez nano-struktury

Streszczenie


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