



A SECOND ORDER LATTICE BOLTZMANN EQUATION TO SIMULATE ELECTRO-DIFFUSION PROBLEMS

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Abstract. *With the increasing interest in miniaturization of devices such as micro-electro-mechanical ones, electrokinetic flows in diminute scales have received a lot of attention. Here, a second order lattice Boltzmann equation is proposed and a Chapman – Enskog expansion shows it correctly retrieves the Nernst-Planck equation. The electrical potential is solved via a Poisson Solver and the simulations found a very good agreement with analytical solutions for steady state electro-diffusion.*

Keywords: *lattice Boltzmann second order equation, electro-diffusion flows, Chapman-Enskog expansion, Poisson, Nernst-Planck*

1. INTRODUCTION

Electrokinetic flows in micro and nano scales have become a relevant topic in the last decades in applications in micro electro-mechanical and biochemical devices, such as micro-mixers and micro-pumps (Lin and Chen, 2013), lab on a chip (Guo et al., 2005), micro-batteries (Liu and Yang, 2009), and fuel cells (He and Li, 2000). Also, biological cells are immersed in an electrochemical environment and the electrokinetic flows form the basis for the physiology at cellular level (Park et al., 2006, He and Li, 2000).

Most applications of interest involve the mass transport in a multi-component mixture subjected to short-range electrostatic interaction and, in some applications, chemical reactions and energy transfer (Wang and Kang, 2010). These phenomena are characterized by different geometric and phenomenological time and length scales that span many orders of magnitude. Since important non-equilibrium phenomena occur at the micro and nano scales, a single macroscopic approach might be insufficient to capture the relevant interactions. On the other extreme, molecular dynamic simulations are expensive when the physical domain extends beyond a few molecules (Zhang, 2011; Melchionna and Marconi, 2011; Horbach and Frenkel, 2001; Horbach, 2003). A common approach is the use of multi-scale computational treatment, combining different physical models (Capuani et al., 2004).

Alternatively, the Lattice Boltzmann method (LBM) seems very promising. The LBM has been developed as a numerical scheme for modeling physics of fluids and simulating fluid flows in applications involving interfacial dynamics and complex geometries. The fundamental idea of LBM is to construct simplified kinetic models that incorporate the essential physics of microscopic and mesoscopic processes so that macroscopic averaged properties obey the desired macroscopic equations (Chen and Doolen, 1998). In LBM, the microscopic information is used to model the mesoscopic dynamics of pseudo-particles. Thus, the LBM can be understood as a mesoscopic approximation of the Boltzmann equation, applicable to condensed matter (He and Luo, 1997; Philippi et al, 2006; Shan et al., 2006).

In this work, we are interested in the simulation of the mass transport in diluted solutions of ions in isothermal conditions without any effects of magnetic field and polarizations. A Lattice Boltzmann second order equation is proposed and, using a Chapman-Enskog expansion, the macroscopic Nernst-Planck equation is recovered. Analytical solutions for steady state electro-diffusion are used to validate the proposed equation.

In the following, initially, the macroscopic equations for electro-kinetic flows are presented.

2. MACROSCOPIC TREATMENT OF ELECTROKINETIC FLOWS

The Nernst-Planck equation models the time and space evolution of the molar concentration of an ionic chemical species i , $C^{(i)}(\vec{x}, t)$, and may be written as

$$\frac{\partial C^{(i)}}{\partial t} + \frac{\partial C^{(i)} \vec{u}}{\partial \vec{x}} = \frac{\partial}{\partial \vec{x}} \left(D_{efe}^{(i)} \frac{\partial C^{(i)}}{\partial \vec{x}} + \frac{z^{(i)} e_0}{kT} D_{efe}^{(i)} \frac{\partial}{\partial \vec{x}} \left(C^{(i)} \frac{\partial V}{\partial \vec{x}} \right) \right), \quad (1)$$

where \vec{u} is the mixture velocity; $D_{efe}^{(i)}$ is the molecular mass diffusivity of ion i in the mixture, $z^{(i)}$ is the ion valence; e_0 is the proton charge; k is the Boltzmann constant and T is the absolute temperature.

Assuming that the mixture is a Newtonian, incompressible fluid, the fluid dynamics of the mixture may be modeled using the continuity and the Navier-Stokes equation that can be written as

$$\frac{\partial \vec{u}}{\partial \vec{x}} = 0, \quad (2)$$

$$\frac{\partial \vec{u}}{\partial t} + \vec{u} \cdot \frac{\partial \vec{u}}{\partial \vec{x}} = -\frac{\partial p}{\partial \vec{x}} + \frac{\partial}{\partial \vec{x}} \left(\nu \frac{\partial \vec{u}}{\partial \vec{x}} \right) + \vec{F}, \quad (3)$$

where ρ is the mixture mass density; p is the pressure; ν is the mixture kinematic viscosity and \vec{F} is the body force per unit volume. In the case of electrokinetic flows, the effect of the external electrical field is included in this term.

Finally, the Poisson equation relates the electrical potential with the volumetric charge density as,

$$\frac{\partial^2 V}{\partial x^2} = -\frac{\rho_e}{\epsilon_r \epsilon_0} = -\frac{e_0 A_v}{\epsilon_r \epsilon_0} \sum_i z^{(i)} C^{(i)}, \quad (4)$$

where ϵ_r is the dimensionless mixture dielectric constant; ϵ_0 is the permittivity of vacuum; ρ_e is the net charge density and A_v is the Avogadro number.

Equations (1) to (4), completed by an equation of state and the appropriate boundary and initial conditions, are a closed-form system of equations for the solution of $C^{(i)}$, \vec{u} , p and V .

3. REVIEW OF PREVIOUS WORK ON LBM

He and Li (2000) studied electrochemical systems with the hypothesis of electroneutrality. This means that the right hand side of Eq. (4) vanishes simplifying it to a Laplace equation. Advection was neglected and both, Laplace and Nernst-Planck equations were solved using LBM. The proposed LB equation for the Nernst-Planck equation has first order accuracy. They introduced chemical reactions at the boundaries inducing the formation of an electrical double layer.

Wang and Kang (2010), by the other hand, assumed the validity of the steady state solution of the Nernst-Planck equation. They also neglected the advection term. Using these assumptions, the Nernst Planck equation becomes equal to the Boltzmann distribution,

$$C^{(i)} = C_c^{(i)} \exp\left(-\frac{e_0 z^{(i)} V}{kT}\right), \quad (5)$$

where $C_c^{(i)}$ is a boundary condition applied at $x = 0$.

In this case, Eqs. (1) and (4) decouple. Substituting Eq. (5) in Eq.(4), the Poisson-Boltzmann equation is obtained,

$$\frac{\partial^2 V}{\partial x^2} = -\frac{e_0 A_v}{\epsilon_r \epsilon_0} \sum_i z^{(i)} C_c^{(i)} \exp\left(-\frac{e_0 z^{(i)} V}{kT}\right). \quad (6)$$

This approach is commonly applied to study electro-osmotic flows. In this situation, the flow is completely described by the Poisson-Boltzmann and the Navier-Stokes equations. These formulations are only strictly valid for low velocity, diluted flows. Guo et al. (2005), Wang et al. (2006), Chai and Shi (2007), Chai et al. (2007 a, b) and Lin and Chen (2013) solved both the equation for the mixture and the Poisson Boltzmann equation simultaneously using the lattice Boltzmann approach, i.e., solving both equations via Lattice Boltzmann equations. Guo et al. (2005) and Chai et al. (2007 a) studied non-isothermal electro-osmotic flows and the energy equation was also solved using the LBM. Wang et al (2006) included the Boltzmann factor inside the equilibrium distribution of the mixture for accounting the influence of a conservative force field. They used such approach to analyze the electrical double layer formed in microchannels. Lin and Chen (2013) analyzed the influence of different patterns of external potential fields and also pressure fields in the improvement of mixer devices. Chai et al. (2007 b) studied electro-osmotic flows in porous microchannels.

Liu and Yang (2009) introduced the effect of ion size, ion volume and image effects (dielectric constant discontinuity at the wall) into the Poisson-Boltzmann distribution to analyze the energy conversion in nanobatteries. The equilibrium distribution function of the mixture was developed until sixth order but the modified Poisson-Boltzmann equation was not solved via LB. Li and Kwok (2003) used the Boltzmann factor into the equilibrium distribution of the mixture (as done later by Wang et al, 2006) to analyze the formation of the electrical double layer in microchannels submitted by external electrical forces. They applied this equation in fully developed velocity profile problems obtaining directly the electrical potential. Horbach (2003) and Horbach and Frenkel (2001) introduced a term of macro-ions charge into the Poisson Boltzmann distribution to analyze the transport of charged colloids. They solved the Poisson Boltzmann equation by a Successive-Over-Relaxation method.

For unsteady-state problems there is the necessity to solve the evolution of ions concentrations. Literature on the subject is limited. For example, we can mention the works of Park et al. (2006) and Wang and Kang (2010). Both presents three Lattice Boltzmann equations, i.e., for the electrical potential, ions and mixture to study electrokinetic flows. While the evolution equation for the ions concentrations proposed by Park et al (2006) was first order only, the Wang and Kang (2010) proposition involves the calculation of many derivatives, which can be a source of errors (Lee and Lin, 2005). A kinetic equation for ions concentration was proposed by Melchionna and Marconi (2011) that recovers a macroscopic equation not limited by the advection of the mixture, i.e., the equation is not limited to dilute solutions. The discretization procedure was the same as the one proposed by Guo et al (2002) and the Poisson equation was solved by the Successive-Over-Relaxation method.

In this work, a Lattice Boltzmann equation of second order accuracy that correctly retrieves the Nernst-Planck equation is derived being simpler than the one proposed by Melchionna and Marconi (2011), because is applied only to dilute solutions. With exception of the later all the above methods that solve the transient ion concentration (Park et al., 2006; Wang and Kang, 2010 and He and Li, 2000) are first order accurate.

4. SECOND-ORDER ACCURATE LATTICE BOLTZMANN MODEL

In this section we propose a Lattice Boltzmann equation for solving the transport of ions in a dilute solution. The proposed equation is second order accurate, avoiding the discretization errors related to the forcing terms.

Operationally, the standard LB method can be described as follows. First, the physical space is discretized in a uniform, square lattice. Then, the particle velocity space is also discretized in l directions, such that there are $k = 0, 1, 2, \dots, l$ possible microscopic velocities, including the zero velocity state ($k = 0$). The particle density distribution for each population moving in the k direction is approximated by the particle distribution function $f_k^{(p)}$. From a numerical point of view, the solution of the LBE is obtained from a finite difference discretization scheme. The first-order backward Euler scheme is chosen for the transient term while the first-order upwind scheme is chosen for the convective term. In a fixed grid, fixed time-step scheme, the resulting discretized for of the LBE becomes

$$f_k^{(p)+} - f_k^{(p)} = \frac{1}{2} \Delta t^{(p)} \left(\Omega_{sd,k}^{(p)} + \Omega_{ld,k}^{(p)} + \Omega_{sd,k}^{(p)+} + \Omega_{ld,k}^{(p)+} \right), \quad (7)$$

where $f_k^{(p)}$ is the distribution function of species (p) at the location \vec{x} and time t and the superscript + represents the distribution function at $\vec{x} + \vec{\xi}_k \Delta t^{(p)}$ and time $t + \Delta t^{(p)}$, where $\vec{\xi}_k$ is the discrete velocity and $\Delta t^{(p)}$ is the numerical time step. The subscript k represents the directions of the lattice velocities.

In Eq. (7), $\Omega_{sd,k}^{(p)}$ is the short distance collision term and $\Omega_{ld,k}^{(p)}$ is a long distance collision term. The collision terms describe the interactions among the particles. In the case of a dilute solution, the short-range collision term contains the interaction between the ion of species (p) and the solute. The long-range collision term represents the collisions between species (p) and the other ions. The electrical potential develops as the result of the long-range collision term. These collision terms are modeled as

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$$\begin{aligned}
 \Omega_{sd,k}^{(p)} &= \frac{1}{\Delta t^{(p)}} \frac{f_{k,eq}^{(p)} - f_k^{(p)}}{\tau^{(p)}}, \\
 \Omega_{sd,k}^{(p)+} &= \frac{1}{\Delta t^{(p)}} \frac{f_{k,eq}^{(p)+} - f_k^{(p)+}}{\tau^{(p)}}, \\
 \Omega_{ld,k}^{(p)} &= -f_{k,eq}^{(p)} z^{(p)} e_0 \frac{(\vec{\xi}_k - \vec{u})}{kT} \cdot \frac{\partial V}{\partial \vec{x}}, \\
 \Omega_{ld,k}^{(p)+} &= -f_{k,eq}^{(p)+} z^{(p)} e_0 \frac{(\vec{\xi}_k - \vec{u}^+)}{kT} \cdot \frac{\partial V^+}{\partial \vec{x}},
 \end{aligned} \tag{8}$$

where $\tau^{(p)}$ is the dimensionless relaxation time of the species (p) and $f_{k,eq}^{(p)}$ is the Maxwellian equilibrium distribution function.

The equilibrium distribution function approximates the Maxwell-Boltzmann molecular velocity distribution and must recover the macroscopic flow variables when it is integrated over the velocity space. Since the lattice only allows for discrete velocities, the integration becomes a quadrature problem (Philippi et al., 2006; Shan et al., 2006), i.e., to find a set of discretized velocities and quadrature weights such that all the desired macroscopic moments are exactly retrieved as moments of the discrete equilibrium distribution function. Here, following second order Gauss-Hermite quadrature (Philippi et al, 2006), the discrete equilibrium distribution function is written as:

$$f_{k,eq}^{(p)} = w_k C^{(p)} \left(1 + \frac{\xi_k u}{RT} + \frac{(\xi_k u)^2}{2(RT)^2} - \frac{u^2}{2RT} \right), \tag{9}$$

where R is the universal gas constant and w_k represents the weight coefficients related with the chosen lattice.

In general, higher order discretizations are needed to non-isothermal problems (Philippi et al, 2006). However, schemes based on nine micro-velocities are sufficient to recover the physics of isothermal flows. For a D2Q9 lattice (a two dimensional, nine velocities, lattice) the weights are:

$$w_k = \begin{cases} 4/9 & \text{for } k = 0, \\ 1/9 & \text{for } k = 1, 2, 3, 4, \\ 1/36 & \text{for } k = 5, 6, 7, 8. \end{cases} \tag{10}$$

The macroscopic variable, $C^{(p)}$, is found as the zeroth moment of the distribution function, i.e.,

$$C^{(p)} = \sum_k f_k^{(p)}. \tag{11}$$

In the next section, the Chapman-Enskog expansion is applied on Eq. (7) recovering the Nernst-Planck equation, Eq. (1). The electrical potential is solved using the Chai and Shi (2008) method and the derivatives that appear on Eq. (8) are approximated using the method developed by Lee and Lin (2005). We focus on electro-diffusion problems where the influence of advection is negligible, and thus, the fluid dynamic equations (continuity and Navier-Stokes) for the solute are not solved.

5. CHAPMAN-ENSKOG EXPANSION

Initially, the following non-dimensional variables are defined:

$$\begin{aligned}
 \vec{\xi}_k^* &= \vec{\xi}_k \frac{\Delta t^{(p)}}{\Delta x}, & \vec{u}^* &= \vec{u} \frac{\Delta t^{(p)}}{\Delta x}, \\
 \epsilon &= \frac{\Delta x}{L}, & \chi &= \frac{\Delta t^{(p)}}{\Gamma}, \\
 \vec{x}^* &= \frac{\vec{x}}{L}, & t^* &= \frac{t}{\Gamma}.
 \end{aligned} \tag{12}$$

The distribution $f_k^{(p)}$ and the time derivative are asymptotically expanded according to

$$f_k^{(p)} = f_{k,0}^{(p)} + \epsilon f_{k,1}^{(p)} + \epsilon^2 f_{k,2}^{(p)} + \dots, \quad (13)$$

and

$$\frac{\partial}{\partial t^*}(\) = \frac{\partial}{\partial t_0^*}(\) + \epsilon \frac{\partial}{\partial t_1^*}(\) + \epsilon^2 \frac{\partial}{\partial t_2^*}(\) + \dots \quad (14)$$

So, also expanding the distribution function $f_k^{(p)+}$ and the collision term $\Omega_k^{(p)+}$ in a Taylor series up to the second order we obtain:

$$\begin{aligned} & \frac{\chi}{\epsilon} \frac{\partial f_{k,0}^{(p)}}{\partial t_0^*} + \chi \frac{\partial f_{k,1}^{(p)}}{\partial t_0^*} + \chi \frac{\partial f_{k,0}^{(p)}}{\partial t_1^*} + \bar{\xi}_k^* \cdot \frac{\partial f_{k,0}^{(p)}}{\partial \bar{x}^*} + \epsilon \bar{\xi}_k^* \cdot \frac{\partial f_{k,1}^{(p)}}{\partial \bar{x}^*} + \frac{1}{2} \frac{\chi^2}{\epsilon} \frac{\partial}{\partial t_0^*} \frac{\partial f_{k,0}^{(p)}}{\partial t_0^*} + \\ & + \frac{1}{2} \epsilon \bar{\xi}_{k,\alpha}^* \bar{\xi}_{k,\beta}^* \frac{\partial}{\partial x_\alpha^*} \frac{\partial f_{k,0}^{(p)}}{\partial x_\beta^*} + \chi \bar{\xi}_{k,\alpha}^* \frac{\partial}{\partial x_\alpha^*} \frac{\partial f_{k,0}^{(p)}}{\partial t_0^*} = -\frac{1}{\tau^{(p)}} f_{k,1}^{(p)} - \frac{\epsilon}{\tau^{(p)}} f_{k,2}^{(p)} + \\ & + \left(-f_{k,0}^{(p)} z^{(p)} e_0 \frac{(\bar{\xi}_k^* - \bar{u}^*)}{kT} \cdot \frac{\partial}{\partial \bar{x}^*} (V) \right) - \frac{1}{2} \frac{\chi}{\tau^{(p)}} \frac{\partial f_{k,1}^{(p)}}{\partial t_0^*} + \\ & + \left(-\frac{1}{2} \chi \frac{z^{(p)} e_0}{kT} \frac{\partial}{\partial t_0^*} \left(f_{k,0}^{(p)} (\bar{\xi}_k^* - \bar{u}^*) \cdot \frac{\partial}{\partial \bar{x}^*} (V) \right) \right) + \\ & + \left(-\frac{1}{2} \frac{\epsilon}{\tau^{(p)}} \bar{\xi}_{k,\alpha}^* \frac{\partial f_{k,1}^{(p)}}{\partial x_\alpha^*} \right) - \frac{1}{2} \epsilon \frac{z^{(p)} e_0}{kT} \bar{\xi}_{k,\alpha}^* \frac{\partial}{\partial x_\alpha^*} \left(f_{k,0}^{(p)} (\bar{\xi}_k^* - \bar{u}^*) \cdot \frac{\partial}{\partial \bar{x}^*} (V) \right) + \dots \end{aligned} \quad (15)$$

Equation (15) is returned to its physical variables and separated in two equations: One with the terms of order 1, and the other for the terms of order ϵ . Further, the macroscopic moments of such equations are calculated.

5.1 Equation of order 1

The terms of the order of magnitude of 1 in (15) are grouped in a single equation. Returning to the physical variables, such equation can be written as

$$\frac{\partial f_{k,0}^{(p)}}{\partial t_0} + \bar{\xi}_k \cdot \frac{\partial f_{k,0}^{(p)}}{\partial \bar{x}} = -\frac{\epsilon}{\tau^{(p)} \Delta t^{(p)}} f_{k,1}^{(p)} - f_{k,0}^{(p)} z^{(p)} e_0 \frac{(\bar{\xi}_k - \bar{u})}{kT} \cdot \frac{\partial}{\partial \bar{x}} (V). \quad (16)$$

Now, Eq. (16) is summed over k and their first order moments for the ion species p , for the solute and for the mixture are obtained as follows:

- Order 1, first moment:

$$\frac{\partial n^{(p)}}{\partial t_0} + \frac{\partial n^{(p)} u_\alpha}{\partial x_\alpha} = 0. \quad (17)$$

For the mixture, we write

$$\frac{\partial n}{\partial t_0} + \frac{\partial (n u_\alpha)}{\partial x_\alpha} = 0. \quad (18)$$

- Order 1, second moment:

The second moment is found by multiplying Eq (16) by $\bar{\xi}_k^*$ and then summing over k . Returning to the original variables, the second order moment equation is

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$$\begin{aligned} \frac{\partial}{\partial t_0} n^{(p)} u_\beta + \frac{\partial}{\partial x_\beta} \left(\frac{P^{(p)}}{m^{(p)}} \right) + \frac{\partial}{\partial x_\alpha} \left(n^{(p)} u_\alpha u_\beta \right) = -\frac{1}{\tau^{(p)} \Delta t^{(p)}} j_\beta^{(p)} + \\ + \left(-\frac{z^{(p)} e_0}{kT m^{(p)}} \left(P^{(p)} \frac{\partial V}{\partial x_\beta} \right) \right). \end{aligned} \quad (19)$$

Summing over all components, c , the second order moment for the mixture is found as

$$\frac{\partial}{\partial t_0} n u_\beta + \frac{\partial}{\partial x_\beta} \left(\sum_c \frac{n^{(c)} kT}{m^{(c)}} \right) + \frac{\partial}{\partial x_\alpha} \left(n u_\alpha u_\beta \right) = -e_0 \frac{\partial V}{\partial x_\beta} \sum_c z^{(c)} \frac{n^{(c)}}{m^{(c)}}. \quad (20)$$

5.2 Equation of order \in

The same procedure is applied to the terms of order \in :

- Order \in , first moment:

$$\in \frac{\partial}{\partial t_1} n^{(p)} + \frac{\partial}{\partial x_\alpha} j_\alpha^{(p)} = 0. \quad (21)$$

Finally the macroscopic equations and the diffusive term can be obtained.

5.3 Mass conservation equation

The mass conservation equation can be found by summing (17) and (21):

$$\frac{\partial n^{(p)}}{\partial t} + \frac{\partial n^{(p)} u_\alpha}{\partial x_\alpha} = -\frac{\partial}{\partial x_\alpha} j_\alpha^{(p)}. \quad (22)$$

5.4 Mass diffusive flux

In order to find the mass diffusive flux, the left hand side of Eq. (16) is developed obtaining:

$$j_\alpha^{(p)} = -\tau^{(p)} \Delta t^{(p)} \frac{kT}{m^{(p)}} \left(\frac{\partial n^{(p)}}{\partial x_\alpha} \right) - \tau^{(p)} \Delta t^{(p)} z^{(p)} e_0 \frac{n^{(p)}}{m^{(p)}} \left(\frac{\partial V}{\partial x_\alpha} \right). \quad (23)$$

Finally, substituting (23) into(22), one obtains:

$$\frac{\partial n^{(p)}}{\partial t} + \frac{\partial n^{(p)} u_\alpha}{\partial x_\alpha} = \frac{\partial}{\partial x_\alpha} \left[\tau^{(p)} \Delta t^{(p)} \frac{kT}{m^{(p)}} \left(\frac{\partial n^{(p)}}{\partial x_\alpha} \right) + \tau^{(p)} \Delta t^{(p)} z^{(p)} e_0 \frac{n^{(p)}}{m^{(p)}} \left(\frac{\partial V}{\partial x_\alpha} \right) \right]. \quad (24)$$

Comparing (24) to (1) and remembering that $C^{(p)} = A_p n^{(p)}$, the effective mass diffusivity of the pair (p - solute) is found:

$$D_{efe}^{(p)} = \frac{\Delta t^{(p)} \tau^{(p)} kT}{m^{(p)}}. \quad (25)$$

With that we proved that Eq. (7) recovers the Nernst Planck equation.

It should be noticed that in the development above, it was assumed the following identity between the moments in the discrete and continuous equilibrium distributions:

$$\sum_k f_{k,eq}^{(p)} \Phi(\vec{\xi}_k) = \int f_{MB}^{(p)} \Phi(\vec{\xi}) d\vec{\xi} \quad (26)$$

where $\Phi(\vec{\xi}) = 1, \vec{\xi}, \vec{\xi}\vec{\xi}, \dots$ and $\Phi(\vec{\xi}_k)$ is the reciprocal for the discrete distribution.

As we use a D2Q9 lattice, Eq. (26) holds true till the second order moments (Philippi et al, 2006). This means that none non-physical terms are included in the macroscopic equation. Only in electro kinetic problems, where the advection is important, and the fluid dynamics equations for the mixture are solved, these non-physical terms in the local speed would be included. Although, it should not be a problem when such velocity is small.

6. FORMULATION OF TEST PROBLEMS

In this section, Eq. (7) is used together with the electrical potential Lattice Boltzmann solver of Chai and Shi (2008). The later has the following form:

$$g_k^+ - g_k = \frac{g_{eq,k} - g_k}{\tau^V} + \Delta t^V w_k^V \chi D^V, \quad (27)$$

where g_k is the distribution function of the electrical potential at the location \vec{x} and time t ; Δt^V is the numerical time step for this equation; τ^V is the dimensionless relaxation time; χ is the right hand side of (4); w_k^V are weight coefficients (for a D2Q9 lattice w_k^V is equal to 0 for $k=0$ and $1/8$ for $k \neq 0$). The equilibrium distribution function $g_{eq,k}$ is equal to $g_{eq,k} = \bar{w}_k^V V$ (where \bar{w}_k^V is equal to $-8/9$ for $k=0$ and $1/9$ for $k \neq 0$) and D^V is an artificial mass diffusion coefficient defined as:

$$D^V = \frac{1}{3} \Delta t^V c_v^2 \left(\tau^V - \frac{1}{2} \right), \quad (28)$$

where $c_v = \Delta x / \Delta t^V$.

The electrical potential is calculated as

$$V = \sum_{k=1}^8 \frac{9}{8} g_k. \quad (29)$$

For the solution of Eq.(27), the classical propagation – collision algorithm is used. However, Eq. (7) requires more attention because it is an implicit equation both in space and time. In this work, we choose the algorithm proposed by Mattila et al. (2013). As Eqs. (7) and (27) are coupled, they are solved simultaneously in an iteration procedure similar to the one proposed by Wang and Kang (2010). A two dimensional domain is implement with a D2Q9 lattice.

Since the model for the concentration is implicit, there is the need to calculate the derivatives at the neighbor nodes and this can be a problem for nodes near the boundaries. Following Lee and Lin (2005), denoting the coordinates of the notes as points (i,j) the derivative of V with x in a D2Q9 lattice is:

$$\left. \frac{\partial V}{\partial x} \right|_{(i,j)} = \frac{V_{(i+1,j)} - V_{(i-1,j)}}{3\Delta x} + \frac{V_{(i+1,j+1)} - V_{(i-1,j-1)}}{12\Delta x} + \frac{V_{(i+1,j-1)} - V_{(i-1,j+1)}}{12\Delta x} \quad (30)$$

For the boundary at $x = 0$ we adapted the previous calculation to:

$$\left. \frac{\partial V}{\partial x} \right|_{(i,j)} = 2 \frac{V_{(i+1,j)} - V_{(i,j)}}{3\Delta x} + \frac{V_{(i+1,j+1)} - V_{(i,j-1)}}{6\Delta x} + \frac{V_{(i+1,j-1)} - V_{(i,j+1)}}{6\Delta x} \quad (31)$$

For $x = l$, we obtain:

$$\left. \frac{\partial V}{\partial x} \right|_{(i,j)} = 2 \frac{V_{(i,j)} - V_{(i-1,j)}}{3\Delta x} + \frac{V_{(i,j+1)} - V_{(i-1,j-1)}}{6\Delta x} + \frac{V_{(i,j-1)} - V_{(i-1,j+1)}}{6\Delta x} \quad (32)$$

The code is validated using two examples. In both, we compare the steady state solution, i.e., the long elapsed-time solution of Eqs. (7) and (27), with the distributions given by the solution of Eqs. (5) and (6).

6.1 Test problem 1

In the first problem, the Poisson-Boltzmann equation, Eq.(6), is solved using the iterative solver on Maple software. With this distribution, the solution for the concentrations can be easily found from Eq.(5). The convergence criterion is the same of Wang et al. (2010).

A solution with two ions, named A and B , is modeled. The following parameters are applied: $C_c^{(A)} = C_c^{(B)} = C_c = 0.1$ mols/m³; $z^{(A)} = 1$; $z^{(B)} = -1$; $T = 300$ K; $\varepsilon_r = 80$; $\tau^{(A)} = \tau^{(B)} = 1$, $\tau^V = 1$. The problem is one-dimensional with a length of $l = 1 \times 10^{-6}$ m; $\Delta x = 1 \times 10^{-8}$ m; $\Delta t^{(A)} = \Delta t^{(B)} = \Delta t^V = \Delta x$ (the last equality is a consequence of using a regular lattice). The boundary conditions for the electrical potential are $V(0) = V(l) = V_0 = 10$ mV, and, for the ions concentration, we just substitute V_0 into Eq.(5). Figure 1(a) presents the physical domain and the boundary conditions for the test problem 1.

6.2 Test problem 2

With a special choice of the applied parameters and re-writing the Poisson Boltzmann equation in the cgs units system Andrietti et al. (1976) were able to find an analytical solution. We use this solution as a second problem for validation. In such solution, the concentration of ion B for $x \rightarrow \infty$ is half of the concentration of ion A (we used $C_c^{(A)} = 0.1$ mols/m³ and $C_c^{(B)} = 0.05$ mols/m³); $z^{(A)} = 1$; $z^{(B)} = -2$ and $dV/dx|_{x \rightarrow \infty} = 0$. For $x = 0$ a prescribed electrical potential V_0 is used (we used - 25 mV). The other parameters are the same as the previous example.

Figure 1(b) presents the physical domain and the boundary conditions for the test problem 2. The initial conditions for both test problems are a constant distribution equal to the boundary condition at $x = 0$.

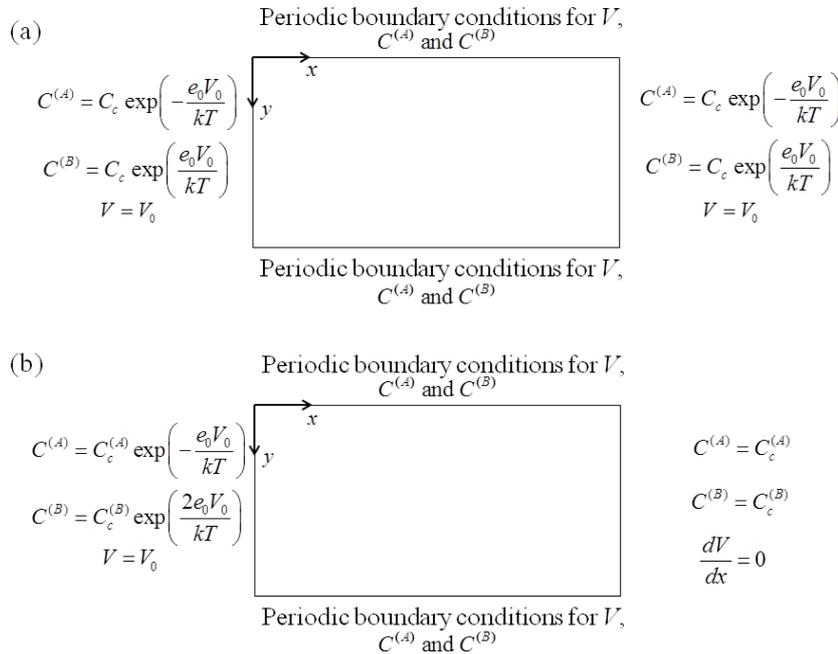


Figure 1. Boundary conditions for (a) test problem 1 and (b) test problem 2.

7. RESULTS AND DISCUSSIONS

Figure 2 presents the results for the test problem 1. The distributions calculated from the Maple solution of the Poisson-Boltzmann equation and the LBM solutions are presented for electrical potential and ion concentration. Both solutions are basically superposed, and the maximum differences are smaller than 3.6% and are found at the boundaries neighbor points ($x/l = 0.01$ and $x/l = 0.99$).

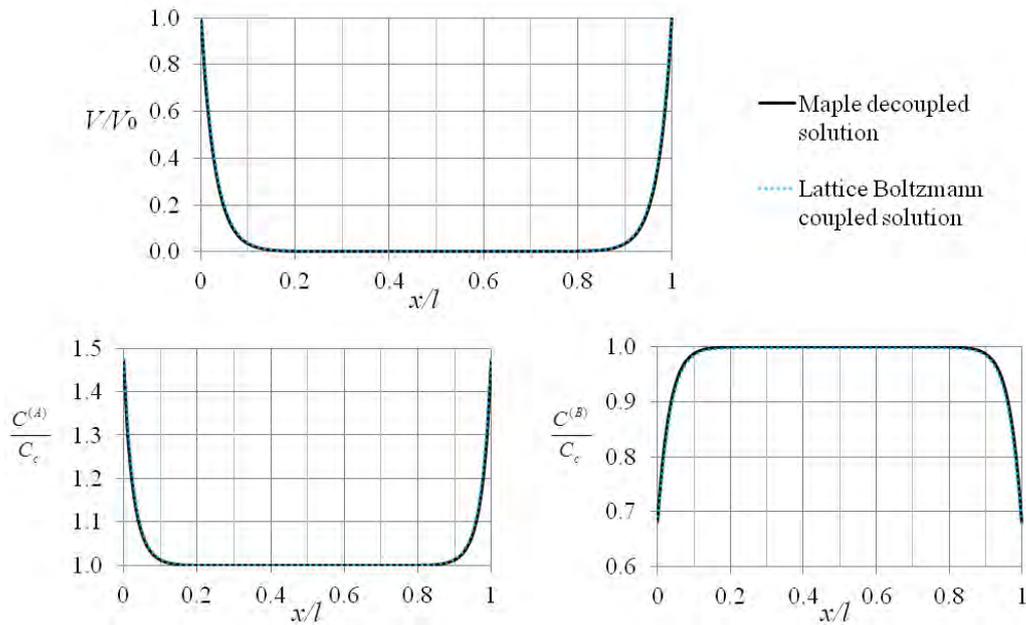


Figure 2. Comparison of the Lattice Boltzmann coupled solution with the decoupled solution using Maple.

Figure 3 presents the results for the test problem 2.

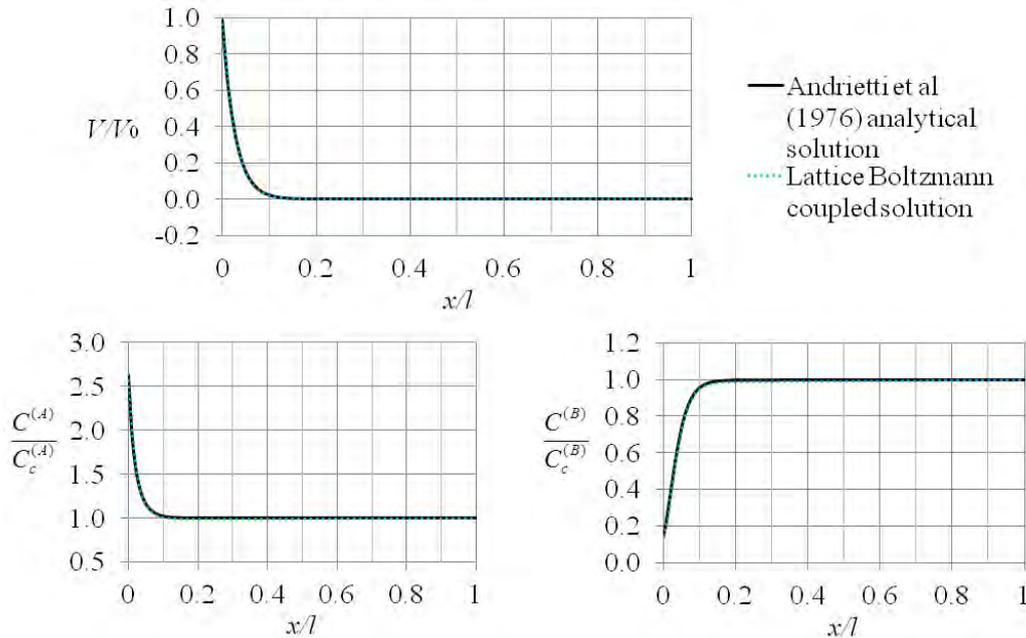


Figure 3. Comparison of the Lattice Boltzmann coupled solution with the analytical solution of Andrietti et al. (1976).

Both solutions are basically identical, and the maximum differences are smaller than 2.66 % and are found at $x/l = 0.01$.

In order to enlarge the difference between the solutions, Fig. 4 presents the relative difference between the electrical potential obtained by the Lattice Boltzmann method and the decoupled solutions for both test problems.

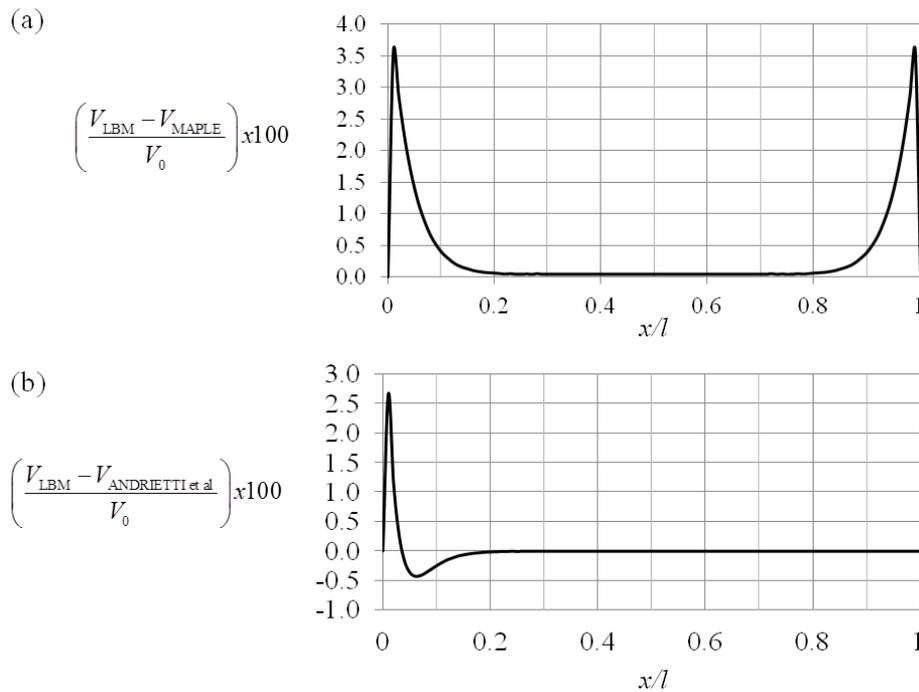


Figure 4. Relative difference of the electrical potential for (a) test problem 1 and (b) test problem 2.

The largest differences occur at the vicinity of the boundaries, especially where the condition of prescribed electrical potential was used. These differences are probably caused by the approximation of the derivative. At the boundaries, we lose precision in calculating the derivatives, mainly when the local profile is steep.

Figure 5 presents the effect of the refinement of the lattice. Test problem 2 was used and the domain was discretized in 20, 50, 100 and 200 lattice-points, respectively. As the problem is one-dimensional (represented by the periodic boundary conditions), we used only 1 node in the vertical axis. Figure 5 presents the relative difference among the LBM solutions and the solution obtained by of Andrietti et al. (1976).

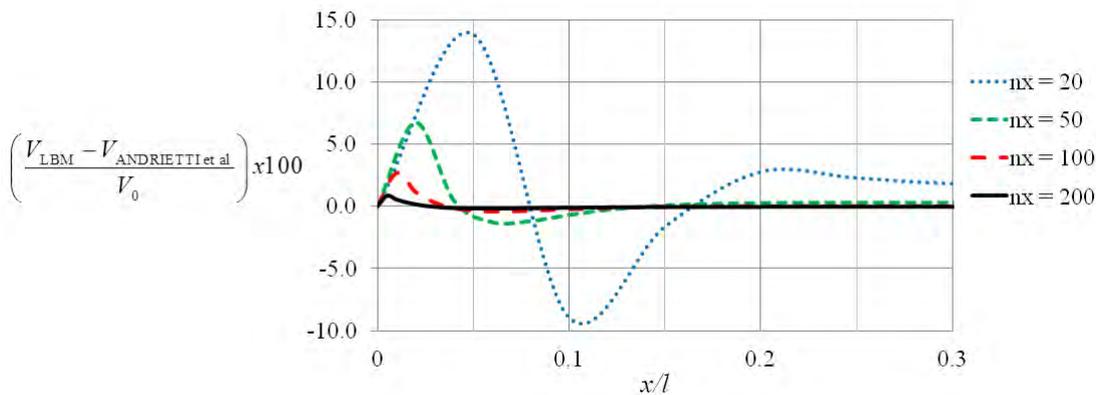


Figure 5. Differences of the electrical potential for different lattice refinement for test problem 2.

It can be noticed that the error is very small for grids with more than 100 points. It is necessary to remember that different grid spacing for the same domain dimension, l , means different diffusivities. Of course, regardless of the derivative calculation, if we are interested only in the steady state solution, this fact will implicate only in the time required to achieve it.

Analyzing the overall results it becomes clear that they are, in general, very close to the analytical solutions. However, it must be remembered that transforming real problems parameters into lattice parameters is usually not trivial. If the effective mass diffusivity of each p -solute pair is different from each other, it could be a cumbersome task to find the right values for the parameters $\Delta t^{(p)}$, $m^{(p)}$ and $\tau^{(p)}$ in Eq.(25). As an illustration, let's say that $D_{efc}^{(p)}$ for an ion p_1 is ten times larger than $D_{efc}^{(p)}$ for an ion p_2 . In this case, for each time step that p_1 is solved, p_2 needs to be solved

ten times. $\Delta t^{(p1)}$ will always be equal to $\Delta t^{(p2)}$, but, the physical meaning attached to each one differs. The problem is even harder to solve if these diffusivities are not multiples of each other. In this case what could be done to circumvent this problem is to choose different values of $\tau^{(p1)}$ and $\tau^{(p2)}$, which could be also difficult because they need to be between 0.5 and 1.5 for stability.

8. CONCLUSIONS

A new second-order accurate Lattice Boltzmann equation to solve diluted solutions of ions was proposed and a Chapman-Enskog expansion showed that it correctly recovers the Nernst-Planck equation. This equation was implemented with the Poisson solver of Chai and Shi (2008). Two steady state solutions for electro-diffusion problems were used to validate the code and a very good agreement was found. Although only problems with no advection were solved, the method is promising for solving fully electrokinetic problems for dissolved ions in solutions.

9. ACKNOWLEDGEMENTS

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