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A multigrid method for the Poisson–Nernst–Planck equations

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ABSTRACT

A computational technique for solving the Poisson–Nernst–Planck (PNP) equations is developed which overcomes the poor convergence rates of commonly used algorithms. The coupled Poisson and charge continuity equations are discretized using an unstructured cell-centered finite volume method. A Newton–Raphson linearization accounting for the coupling between the equations through boundary conditions, and the space charge and drift terms, is developed. The resulting linear system of equations is solved using an algebraic multigrid method, with coarse level systems being created by agglomerating finer-level equations based on the largest coefficients of the Poisson equation. A block Gauss–Seidel update is used as the relaxation method. The method is shown to perform well for the transport of K^+ and Cl^- in a synthetic ion channel for driving voltages, surface charges, ion concentrations and channel aspect ratios ranging over several orders of magnitude.

1. Introduction

Charge transport in the presence of an electric field occurs in a wide variety of modern microsystems, both natural and synthetic. Examples include electro-diffusion and electro-kinesis in biological systems [1,2], nanofluidic diodes [3], in a variety of electro-hydrodynamic (EHD) and ion-driven flows [4,5], and in microelectronics [6]. One area that has received particular attention in recent years is charge transport in ion channels [7–9], which occur in all biological cell membranes. Ion channels are formed by the folding of amino acids to form a water channel through the cell membrane [10]. The side chains of the amino acids can be ionized and can carry permanent charge, the nature and strength of which depends on the solute in which they are immersed. The permeability of the ion channel to specific ions, such as Na^+, K^+, and Cl^-, is controlled by this charge distribution. The regulation of the flow of ions in and out of the cell is critical to maintaining the necessary ion concentrations in the cell. A large community of researchers has performed both experimental and computational investigations of biological ion channels [7–16]. Charge transport also plays a critical role in other biological applications. For example, electro-diffusion is integral to the communication between neurons and muscle fibers, which is mediated by the diffusion of neurotransmitters at synapses and their consumption by hydrolyzation reactions in post-synaptic membranes [2].

With the advent of modern micro- and nano-fabrication processes, interest has focused on the similarity of biological ion channels to microelectronic devices [17–19]. Researchers have sought to mimic biological structures in micro- and nano-electro-mechanical systems (MEMS and NEMS) [19]. In the electronics cooling arena, researchers have exploited similar physics to develop EHD-driven micropumps [4]. Here, the primary pumping mechanism is the drag exerted by charged ions on a solvent fluid by an imposed traveling electric field; charge transport occurs primarily due to the electric field, but may also be assisted by fluid convection.

The Poisson–Nernst–Planck (PNP) equations have widely been used to simulate these classes of ion transport, and with careful modeling, good comparisons with experimental data have been obtained in many instances [12,10]. At extremely small length scales, the PNP approach may be erroneous. The errors stem from treating ions as a continuum fluid and ignoring the discrete interactions of individual ions with the domain boundaries. As the domain scale becomes smaller, the physical volume occupied by the ions and the solvent molecules must be accounted for; failure to do so results in an overestimate of ion density [15]. Researchers have sought to extend the applicability of the PNP approach through the use of corrective potentials [13,14]. The PNP approach is particularly useful in simulating synthetic ion channels where channel diameters, of the order of tens of nanometers [18], are large enough to mitigate the shortcomings of PNP theory. Methods designed to address truly nanoscale domains include Brownian dynamics [15,16], and more recently, molecular dynamics [8,9]. Though these techniques have been shown to yield more accurate results for small-length-scale domains, their cost, particularly for typical biological time scales, has thus far been too great to permit widespread use. As a consequence, PNP theory forms the mainstay of most MEMS and NEMS simulations today.

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Nomenclature

$\mathbf{A}$	area vector, Jacobian matrix
e	electron charge
$\hat{\mathbf{e}}_\mathbf{n}$	outward unit normal vector to face
$\hat{\mathbf{e}}_\mathbf{s}$	unit vector joining cell centroids
$\mathbf{E}$	flux vector
$\mathbf{F}$	drift vector
$\mathbf{J}_p$, $\mathbf{J}_n$	total flux of p and n
k_B	Boltzmann constant
n	number density of negative charges
p	number density of positive charges
$\mathbf{Q}$	solution vector
$\mathbf{R}$	residual vector
$\mathbf{S}$	source vector
T	temperature
V	volume
x, y	Cartesian coordinates

Greek

$\Delta\forall$	volume of control volume
ϵ	relative permittivity
ϵ_0	permittivity of free space
ϕ	potential
Γ	diffusion coefficient
ψ	scalar
σ	surface charge density

Subscripts and superscripts

f	face
0	cell C0
1	cell C1
n	iteration
nb	neighbor

A variety of techniques have been published in the literature to solve the PNP equations. Relatively simple simulation approaches have been taken in the ion channel literature [11,12]. Simple finite difference methods coupled to explicit successive over-relaxation (SOR) schemes have been utilized, with 3-D solutions being published only in the 1990s [12]. Both the Slotboom form [20], which is used to transform the charge transport equations into Laplacians, as well as the primitive Nernst–Planck form, have been used [12]. Reported computational times have been relatively long in these loosely coupled simple iterative techniques, ranging from several minutes to several hours per grid point [12]. More efficient schemes for solving the PNP equations are available in the semiconductor device literature [6,10,14,21–25], where they are referred to as the drift–diffusion equations. But these address much different length scales, and do not, in general, admit geometric complexity since this is not necessary for typical device simulations. Recently, a finite volume scheme coupled to Newton iteration of the underlying non-linear algebraic equations has been implemented in the device simulator PROPHET [10,14,26] and has been used to solve for ion transport in porin channels using a stair-step discretization of the complex pore and membrane geometry [10]. Suitable initial conditions were first generated by solving the Poisson–Boltzmann equation under zero concentration gradients, and continuation techniques were used to incrementally raise the applied bias in order to obtain solutions. Daiguji et al. [18] have reported PNP simulations of synthetic ion channels; however, no details of the underlying computational technique or its performance have been reported. They have also reported simulations coupling the PNP equations to Stokes flow simulations [17], but again, no details of the computational technique have been provided. A hybrid method combining a finite element discretization of the charge continuity equations with a boundary-element simulation of the potential field has been reported in [1,2]; a sequential update of the two equation sets has been reported.

As multigrid methods for the solution of linear algebraic equations reached maturity [27–30], multigrid solutions for the Poisson equation began to appear [21,22]. These simulations provide a robust backbone not only for the PNP equation set, but also for Monte Carlo device simulation. Publications describing multigrid solutions of the entire non-linear PNP equation set (coupling the Poisson with charge continuity) are far less numerous, however. Most published methods only use the multigrid procedure as a linear solver for the individual governing equations. Meza and Tuminaro [23] used a multigrid preconditioner with a conjugate gradient method to solve the Slotboom form [20] of the drift–diffusion equations. They used a Gummel iteration procedure[31], i.e., a sequential solution of each of the PNP equations, for steady state device simulation in the DANCIR code [32]. The resulting solver was shown to be significantly faster and more parallel than that using incomplete lower–upper (ILU) preconditioning. Molenaar [24] employed a mixed finite element discretization of the 2D Poisson and drift–diffusion equations. He used Gummel iteration to resolve non-linearities, and a multigrid procedure for the linear solution of each of the separate PNP equations. The only truly coupled multigrid method we are aware of is the recent work of Clees [25], who developed an algebraic multigrid procedure for a coupled solution of the Poisson and drift–diffusion equations for semiconductor device applications. There has been extensive development of coupled multigrid methods for solving the Navier–Stokes equations in the computational fluid dynamics literature [33–37] which provide guidance on how similar procedures may be developed for the PNP equations.

The objective of this paper is to develop a general, robust, and efficient method for the Poisson–Nernst–Planck equations using an unstructured solution-adaptive finite volume formulation [38]. The method addresses complex geometries, and substantially improves robustness and convergence for strongly non-linear problems and high-aspect-ratio domains through the use of a coupled algebraic multigrid method. The method is verified against a known analytical solution and is found to yield accurate results. It is then applied to the problem of ion transport in a synthetic nanochannel [18] and is shown to perform well for a wide range of operating parameters.

2. Governing equations

The governing equations are the Poisson–Nernst–Planck equations written here for a system of two ion species.

$$\nabla \cdot \epsilon \nabla \phi + \frac{e}{\epsilon_0}(p - n) = 0 \tag{1}$$

$$\nabla \cdot \left(\nabla p + \frac{e \nabla \phi}{k_B T} p \right) = 0 \tag{2}$$

$$\nabla \cdot \left(\nabla n - \frac{e \nabla \phi}{k_B T} n \right) = 0 \tag{3}$$

Here ϕ is the electrostatic potential and p and n are the concentrations of the positively and negatively charged ions, respectively.

Defining the solution vector $\mathbf{Q} \equiv [\phi\ p\ n]^T$, the governing equations can be written in vector form as