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# A conservative discretization of the Poisson–Nernst–Planck equations on adaptive Cartesian grids

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ABSTRACT

In this paper we present a novel hybrid finite-difference/finite-volume method for the numerical solution of the nonlinear Poisson–Nernst–Planck (PNP) equations on irregular domains. The method is described in two spatial dimensions but can be extended to three dimensional problems as well. The boundary of the irregular domain is represented implicitly via the zero level set of a signed distance function and quadtree data structures are used to systematically generate adaptive grids needed to accurately capture the electric double layer near the boundary. To handle the nonlinearity in the PNP equations efficiently, a semi-implicit time integration method is utilized. An important feature of our method is that total number of ions in the system is conserved by carefully imposing the boundary conditions, by utilizing a conservative discretization of the diffusive and, more importantly, the nonlinear migrative flux term. Several numerical experiments are conducted which illustrate that the presented method is first-order accurate in time and second-order accurate in space. Moreover, these tests explicitly indicate that the algorithm is also conservative. Finally we illustrate the applicability of our method in the study of the charging dynamics of porous supercapacitors.



## 1. Introduction

At the continuum level, aqueous electrolytes (e.g. salty water) can be described as conducting liquids. In such a description, the solvent phase is treated as a standard continuum and discrete ions are replaced by continuous concentration fields. Mutual ion–ion interactions, whether steric or electrostatic, are replaced by interactions between ions and a mean-field potential. The simplest of such models is described by the so-called Poisson–Nernst–Planck (PNP) equations [62,27]. The two most important assumptions used in deriving the PNP equations are:

1. ions are effectively point size and thus all steric interactions, due to finite ion size, are absent,
2. ions only interact via a mean-field electrostatic potential field.

Although these assumptions are violated in certain cases [28,7], PNP equations are still very useful in studying many electrochemical and biological phenomena. Examples include, but are not limited to, colloid and interface sciences [62,27],

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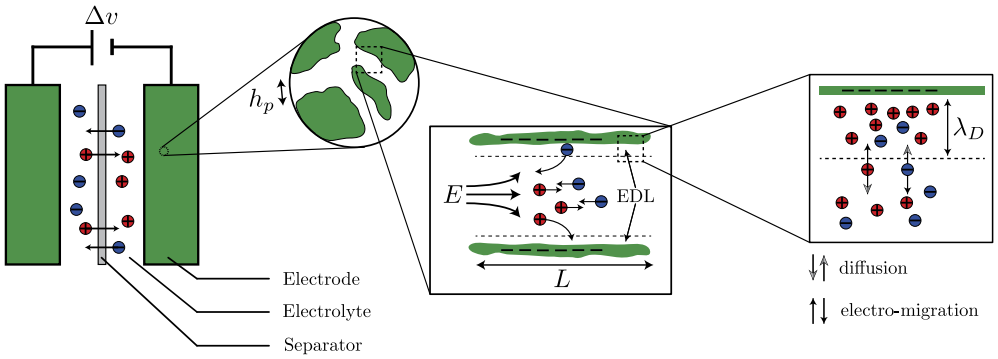


**Fig. 1.** Schematic of a supercapacitor. A supercapacitor is made of two porous electrodes (typically carbon) that are in contact with an electrolyte medium and separated by a separator permeable to ions. Once a potential difference is applied to the electrodes, an electric field is set up that drives ions inside the electrolyte and through pores. This current charges the electrodes by bringing "counter-ions" near to the surface and driving "co-ions" away from the surface. This effectively "screens" the charge on the electrode by creating a thin interfacial layer called electric double layer (EDL). At any given section along the pore, the charging process continues until the diffusion and electro-migration of ions locally reach a balance (see Section 2). At steady state, the work by the external power source is electrostatically stored inside the EDL similar to normal capacitors.

electro-osmosis in micro- and nano-fluidic systems [58,59], electrophoretic motion of charged particles [49,27], computation of solvation energies of biomolecules [37], electro-kinetics of electro-chemical cells [8] and the study of supercapacitors [19].

Although our algorithm is quite general and can be applied, at least partially, to many of the application mentioned above, we will focus on the study of supercapacitor. Supercapacitors are energy storage devices that store electrostatic energy inside a very thin, $\mathcal{O}(10\text{ nm})$, layer, called Electric Double Layer (EDL) [27], which forms at the electrode–electrolyte interface (see Fig. 1). To greatly increase the storage capacity, often porous carbon, or other porous conducting materials, are utilized as the electrode. Here, we do not go into the details of these devices and their applications and refer the interested reader to appropriate references [29,57,39].

In designing supercapacitors, it is important to know the effect of the pore micro-structure; in particular its effect on the charging capacity and the charging time of the device. First theoretical studies of supercapacitors date back to the Transmission-Line (TL) model [21]. The TL model is effectively a one-dimensional, equivalent RC circuit model for individual pores in a porous electrode where each pore is represented as a perfect cylinder. Since its introduction, this linear model has been extensively used in studying [52,29,26] and optimizing supercapacitors [23,48]. Despite its widespread use, the TL model faces serious shortcomings. First, the TL theory is only valid at very small voltages ($< 25$ mV). In real systems however, applied voltages are typically around 1–2.5 V, depending on the electrolyte used [29]. Second, the TL model assumes that the local EDL thickness is much smaller than the pore radius. This condition, although satisfied for wider macro-pores, does not hold at the nano-pores where pore sizes are on the order of, or even smaller than, the Debye layer [57]. Finally, the actual pore micro-structure are explicitly ignored in TL model.

It is possible to address some of the shortcomings of the TL model, e.g. the low voltage applicability and, to some extend, the effects of micro-structure geometry, by utilizing more sophisticated volume-averaging techniques as initially proposed by [47], and later further developed by Bazant and Biesheuvel [11]. Specifically the model proposed in [11], which we shall refer to the BB model from now on, has been recently used to study various aspects of supercapacitors and similar technologies [53,67,61]. Although the BB model is generally a more realistic model than the TL model, it is nonetheless a volume-averaged model and thus has certain shortcomings. For instance, the averaging implicitly assumes a fairly isotropic porous structure; any anisotropy could lead to uneven transport in different directions. Moreover, like the TL model, the BB model is essentially built on the assumption that the EDL is thin compared to a "reference pore dimension". Finally, effects of surface conduction phenomena [27] are completely ignored, *assuming* they are negligible [11].

Despite their popularity, and known shortcomings, very few attempts have been made to directly validate the aforementioned models against a full scale direct numerical simulation (DNS) of the PNP equations at the pore scale. Even the few existing studies are conducted at low voltages; either completely [55] or implicitly for the most part [33]. This is likely due to the numerical challenges associated with the different length scales inherent in the PNP equations at high voltages. In particular, concentration fields often decay exponentially with the local electric potential, which itself decays exponentially with the distance from wall, with a length scale proportional to the EDL thickness [62]. Any successful algorithm must therefore be sophisticated enough to handle such steep gradients efficiently. The PNP equations also involve nonlinear terms describing the flux of ions generated by electric fields. Finally, a useful algorithm, needs to be able to handle the arbitrary and complicated geometry of pore micro-structures (see Fig. 1).

In terms of algorithm development for solving the PNP equations, the biophysics community has been very active. For instance, one-dimensional finite difference methods were utilized by many authors for simulating ion-selective membranes and cellular ion-channels [18,12,32,24,16]. Two- and three-dimension algorithms have also been reported in the literature. In [30,15] authors developed a finite difference, SOR-like algorithm for the steady-state PNP equations. Transient finite difference [68] and finite element [37] methods have also been developed with biophysical applications in mind; though they are general enough that it should be relatively straightforward to apply them to other problems as well. Other communities,