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Comparison and numerical treatment of generalised Nernst–Planck models

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ABSTRACT

In its most widespread, classical formulation, the Nernst–Planck–Poisson system for ion transport in electrolytes fails to take into account finite ion sizes. As a consequence, it predicts unphysically high ion concentrations near electrode surfaces. Historical and recent approaches to an appropriate modification of the model are able to fix this problem. Several appropriate formulations are compared in this paper. The resulting equations are reformulated using absolute activities as basic variables describing the species amounts. This reformulation allows to introduce a straightforward generalisation of the Scharfetter–Gummel finite volume discretisation scheme for drift–diffusion equations. It is shown that it is thermodynamically consistent in the sense that the solution of the corresponding discretised generalised Poisson–Boltzmann system describing the thermodynamical equilibrium is a stationary state of the discretised time-dependent generalised Nernst–Planck system. Numerical examples demonstrate the improved physical correctness of the generalised models and the feasibility of the numerical approach.

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1. Introduction

The motion of an incompressible mixture of $N - 1$ ionic species and an electroneutral solvent component N in the self-consistent electrical field can be described by a system consisting of $N - 1$ Nernst–Planck equations for the motion (relative to the barycentric velocity) of the ions, the Poisson equation for the electrostatic field, and the Navier–Stokes equations for the barycentric velocity of the mixture with a body force depending on the space charge and the electric field. Mostly, throughout the paper, the fluid motion will be regarded in mechanical equilibrium. Electrochemistry and semiconductor devices are two main applications of systems of this type.

The classical drift diffusion approach assumes the species concentration gradient (with a constant diffusion coefficient), the advection by barycentric velocity and the advection by the gradient of the electrostatic potential as driving forces for the motion of charged species in the self-consistent electric field [1]. It is well known for a long time that for electrolytes, this approach fails to reflect the fact that ion sizes are finite. After a first improvement in [2], starting with [3], various volume exclusion models have been proposed to fix this problem with varying generality and success [3–10], see also the reviews of [11,12].

Nonequilibrium thermodynamics [13] suggests that the chemical potentials of the species have to be regarded as driving forces, allowing to describe finite ion size effects in the constitutive relationship between chemical potential and concentration. The authors of [14] recently confirmed that in order to derive a thermodynamically consistent model it is necessary to include the dependency on the pressure into this relationship [4].

In Section 2, the Nernst–Planck–Poisson–Navier–Stokes system for an ideal incompressible mixture is introduced in a formulation equivalent to that provided in [14]. Then, constitutive relationships between chemical potential, pressure and concentration are introduced for four cases: the classical Nernst–Planck equations leading to the Gouy–Chapman double layer model, the excluded volume models after Bikerman and Freise [3,4], the ideal incompressible mixture [14], and – as it is closely related – Fermi–Dirac statistics for semiconductor problems. It is shown that in thermodynamical equilibrium and for the case of equal molar masses, the ideal incompressible mixture model [14] is equivalent to a multispecies generalisation of the Bikerman–Freise model.

In Section 3, with the intention to provide a reliable numerical implementation, the models under investigation are reformulated in absolute activities as basic variables. This reformulation results in a rather simple structure of the resulting system of equations. In particular, cross-coupling of species gradients and degenerating diffusion coefficients are avoided. This formulation as well allows for an easy expression of the equations for thermodynamical equilibrium.

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In Section 4, based on the Scharfetter–Gummel upwind method [15], a finite volume based multi-dimensional numerical approach to the approximate solution of the coupled systems is proposed. It is shown that the discrete solution of the corresponding equilibrium generalised Poisson–Boltzmann problem is a stationary solution of the discretised generalised Nernst–Planck system. Numerical examples demonstrate the features of the different models discussed, and the feasibility of the discretisation.

All notations are listed in Appendix A. Appendix B provides the link of the model described in Section 2 to the formulation used in [14]. In order to support the proposal to formulate the equations in activities as primary variables, Appendix C discusses the consequences of using concentrations as basic unknowns. Appendix D is devoted to the mathematical proof of the existence and uniqueness of the inverse activity coefficients.

2. The Nernst–Planck–Poisson–Navier–Stokes-system

In this section, the Nernst–Planck–Poisson–Navier–Stokes system for an isothermal, incompressible ideal mixture without ion size and solvation effects, representing a solution of $N - 1$ dissolved species characterised by molar densities (in the sequel colloquially referred to as “concentrations”) c_α and molar chemical potentials μ_α in an electroneutral solvent component N is introduced. Different variants for constitutive laws for the chemical potentials are discussed. All notations are found in Appendix A.

For a given distribution of the barycentric velocity \mathbf{v} , the evolution of the molar concentrations c_α of charged species is described by the Nernst–Planck–Poisson system [13,14], see also Appendix B:

$$-\nabla \cdot \varepsilon_0 \varepsilon_r \nabla \phi = q, \quad (2.1a)$$

$$\partial_t c_\alpha + \nabla \cdot (c_\alpha \mathbf{v} + \mathbf{N}_\alpha) = 0 \quad (\alpha = 1 \dots N - 1), \quad (2.1b)$$

$$\mathbf{N}_\alpha = -\frac{D_\alpha}{RT} c_\alpha \left(\nabla \mu_\alpha - \frac{M_\alpha}{M_N} \nabla \mu_N + z_\alpha F \nabla \phi \right) \quad (\alpha = 1 \dots N - 1). \quad (2.1c)$$

In the effective chemical potentials (also called “entropy variables” [16])

$$\tilde{\mu}_\alpha = \mu_\alpha - \frac{M_\alpha}{M_N} \mu_N \quad (\alpha = 1 \dots N - 1) \quad (2.2)$$

the Nernst–Planck equation (2.1c) rewrites as

$$\mathbf{N}_\alpha = -\frac{D_\alpha}{RT} c_\alpha (\nabla \tilde{\mu}_\alpha + z_\alpha F \nabla \phi) \quad (\alpha = 1 \dots N - 1). \quad (2.3)$$

By their very definition [13], the N diffusion fluxes $\mathbf{J}_\alpha = M_\alpha \mathbf{N}_\alpha$ are defined relative to the barycentric velocity \mathbf{v} and sum up to zero, yielding a condition to define the solvent flux \mathbf{J}_N . There is no independent equation for \mathbf{J}_N of the form (2.1c). The solvent concentration

$$c_N = \bar{c} - \sum_{\alpha=1}^{N-1} c_\alpha \quad (2.4)$$

is the difference between the constant mixture concentration \bar{c} and the sum of the concentrations of the dissolved species.

The evolution of the velocity field is described by the incompressible Navier–Stokes equations for the barycentric velocity \mathbf{v} and the pressure p under a body force exerted by the motion of ions:

$$\partial_t (\rho \mathbf{v}) + \nabla \cdot (\rho \mathbf{v} \otimes \mathbf{v}) - \eta \Delta \mathbf{v} + \nabla p = -q \nabla \phi \quad (2.5a)$$

$$\partial_t \rho + \nabla \cdot (\rho \mathbf{v}) = 0 \quad (2.5b)$$

$$\rho = M_N \bar{c} + \sum_{\alpha=1}^{N-1} (M_\alpha - M_N) c_\alpha \quad (2.5c)$$

The density ρ depends on the local composition of the mixture. In general it is not constant in space and time. Only in the case of equal molar masses the incompressibility constraint $\bar{c} = \text{const}$ (B.5) (see also Appendix B.2) coincides with $\rho = \text{const}$. Only this case would allow to turn (2.5b) into the condition $\nabla \cdot \mathbf{v} = 0$ which often is seen as synonymous with incompressibility.

From [13], replacing specific quantities by molar ones, one obtains the Gibbs–Duhem relation

$$\sum_{\alpha=1}^N c_\alpha \nabla \mu_\alpha = \nabla p. \quad (2.6)$$

Following [13], system (2.1) is said to be in *mechanical equilibrium* if $\partial_t \mathbf{v} = 0$ and $\nabla \cdot \mathbf{v} = 0$. If, in addition, $\mathbf{N}_\alpha = 0$ for $\alpha = 1 \dots N$, then system (2.1) is said to be in *thermodynamical equilibrium*.

In the case of mechanical equilibrium, the Navier–Stokes equations (2.5) reduce to the force balance [13]

$$\nabla p = -q \nabla \phi. \quad (2.7)$$

Taking the divergence on both sides of (2.7) gives

$$-\Delta p = \nabla \cdot q \nabla \phi. \quad (2.8)$$

As it can be assumed that far from an electrode, the pressure p can be set equal to a fixed reference pressure p° , (2.8) is a variant of the force balance (2.7) which leads to a second order partial differential equation for the pressure p which can be treated by standard analytical and numerical tools.

In order to close system (2.1), it is necessary to introduce constitutive relationships between the chemical potentials $\mu_1 \dots \mu_N$ and the other quantities.

2.1. Chemical potential for classical Nernst–Planck theory

In this theory, it is assumed that the motion of the solvent is not influenced by the motion of the dissolved species, and the chemical potential can be set according to [17]. The chemical potential of the solvent is set to $\mu_N = 0$, leading to $\tilde{\mu}_\alpha = \mu_\alpha$ for $\alpha = 1 \dots N - 1$. It is then assumed that the chemical potential follows the ansatz for an ideal gas:

$$\tilde{\mu}_\alpha^{\text{GC}} = \mu_\alpha = \mu_\alpha^\circ + RT \ln \frac{c_\alpha}{\bar{c}} \quad (\alpha = 1 \dots N - 1). \quad (2.9)$$

It corresponds to the Gouy–Chapman double layer model [18] and is therefore labelled as “GC”. This ansatz regards ions as point charges and misses the fact that the finite size of real ions limits the maximum possible species concentrations c_α . In [14] it has been criticised for not being consistent to the approach of non-equilibrium thermodynamics.

2.2. Chemical potential for excluded volume models

The deficiencies of the model (2.9) have been known since a long time, and the introduction of an excluded volume constraint is the subject of a significant number of papers, e.g. [3–10]. See also the reviews of [11,12].

The summary volume fraction of the dissolved species amounts to

$$\Phi = \sum_{\alpha=1}^{N-1} v_\alpha c_\alpha, \quad (2.10)$$

where v_α is the partial molar volume necessary to accommodate 1 mol of species α together with the hydration shells [11]. Given

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