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Transport of charged particles: Entropy production and Maximum Dissipation Principle

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A B S T R A C T

In order to describe the dynamics of crowded ions (charged particles), we use an energetic variational approach to derive a modified Poisson–Nernst–Planck (PNP) system which includes an extra dissipation due to the effective velocity differences between ion species. Such a system has more complicated nonlinearities than the original PNP system but with the same equilibrium states. Using Galerkin's method and Schauder's fixed-point theorem, we develop a local existence theorem of classical solutions for the modified PNP system. Different dynamics (but same equilibrium states) between the original and modified PNP systems can be represented by numerical simulations using finite element method techniques.

1. Introduction

The dynamics of ion transport is important for the study of biophysics as it is involved in almost all biological activities. The transport of charged particles (ions), by nature, is a multiscale problem. The competition of thermal fluctuation, in terms of entropy, and molecular (Coulomb) interactions mainly give intriguing and significant behaviors of the systems. Choices of the variables, in terms of energetic functionals and entropy production (dissipation) functionals, demonstrate specific physical situations or applications in consideration. By employing an energetic variational approach (see Section 2.1), we can derive the original Poisson–Nernst–Planck (PNP) system (see Section 2.2) which describe dilute ionic liquids [20–22].

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The transport of ions in biological environments are usually in non-ideal situations. Ion channels often have characteristic property of very high density distributions of ions that are crowded into tiny spaces with huge electric and chemical fields and forces of excluded volume (cf. [6–8]). To describe the dynamics of crowded ions, the energy functional and the dissipation functional should be modified. For the energy functional, we combined the energy functional of the original PNP system with Lennard-Jones type (LJ) potential (similar to those used for molecular dynamic simulations) and derive new PNP-type systems which captured certain properties of selectivity of ion channels (cf. [9,12,14,17]).

The dynamical systems for transport of ions involve various types of entropy production. The classical PNP equation involves the entropy production, the dissipation, in terms of sum of damping due to individual ion species. In this study, we take into consideration of the extra dissipation due to a drag force between different species. This extra dissipative effect, due to the drag between ion species, is incorporated into the derivation of a modified PNP system. The entropy production of modified PNP mainly contributes to the dynamics of the system, while the equilibrium states, which are determined by the free energy, remain the same. In other applications of physics, such consideration had been taken into account in the study of ion heating in a plasma flow (cf. [5]).

The modified PNP system has more complicated nonlinearities than the original PNP system but with the same equilibrium states. Using Galerkin's method and Schauder's fixed-point theorem, we develop a local existence theorem of classical solutions for the modified PNP system. Furthermore, different dynamics (but same equilibrium states) between the original and modified PNP systems can be represented by numerical simulations using finite element method techniques.

The rest of this paper is organized as follows: In Section 2, we derive the modified PNP system. The local existence of the modified PNP system is proved in Section 3. In Section 4, we provide numerical results of the modified PNP system and comparisons to those of the original PNP system.

2. General diffusion for transport of charged particles

In this section, we firstly introduce the energetic variation framework for diffusions and then apply it to derive the original PNP system. Such a framework can be employed to the problem of transport of ions in non-ideal, non-diluted situations. We derive a modified PNP system that takes into account of additional dissipation due to the effect of velocity differences between ion species.

2.1. Energetic variational approaches for diffusion

For an isothermal closed system, the combination of the First Law and the Second Law of Thermodynamics yields the following energy dissipation law:

$$\frac{d}{dt}E^{\text{total}} = -\triangle, \tag{2.1}$$

where E^{total} is the sum of kinetic energy and total Helmholtz free energy, and $\triangle$ is the entropy production (energy dissipation rate in this case). The choice of total energy functional and dissipation functional, together with the kinematic (transport) relation of the variables employed in the system, determines all the physics and the assumptions for problem.

The energetic variational approach is the precise framework to obtain the force balance equations from the general dissipation law (2.1). In particular, the Least Action Principle (LAP) will determine the Hamiltonian part of the system and the Maximum Dissipation Principle (MDP) for the dissipative part. Formally, LAP states the fact that force multiplies distance is equal to the work, i.e.,

$$\delta E = \text{force} \times \delta x, \tag{2.2}$$