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Field Model for Complex Ionic Fluids: Analytical Properties and Numerical Investigation

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Abstract. In this paper, we consider the field model for complex ionic fluids with an energy variational structure, and analyze the well-posedness to this model with regularized kernels. Furthermore, we deduce the estimate of the maximal density function to quantify the finite size effect. On the numerical side, we adopt a finite volume scheme to the field model, which satisfies the following properties: positivity-preserving, mass conservation and energy dissipation. Besides, series of numerical experiments are provided to demonstrate the properties of the steady state and the finite size effect by showing the equilibrium profiles with different values of the parameter in the kernel.

AMS subject classifications: 35Q92, 65M08, 65M12, 92E20

Key words: Complex ionic fluids, variational structure, finite size effect, finite volume method.

1 Introduction

Nearly all biological processes are related to ions [7]. The electrokinetic system for ion transport in solutions is an important model in medicine and biology [1,4]. The transport and distribution of charged particles are crucial in the study of many physical and biological problems, such as ion particles in the electrokinetic fluids [14], and ion channels in cell membranes [3,8]. In this paper, we consider the field equations for complex ionic fluids derived from an energetic variational method EnVarA (energy variational analysis)

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which combines Hamilton's least action and Rayleigh's dissipation principles to create a variational field theory [7].

In EnVarA, the free energy of the field systems which is denoted by $\mathcal{F}$ for complex ionic fluids is written in the Eulerian framework

$$\mathcal{F}(c_m(\cdot,t)) = \int_\Omega \left\{ \sum_{m=1}^{M} c_m \log c_m + \phi_{\rm ES}(\cdot) + \psi_{\rm FSE}(\cdot) \right\} \mathrm{d}\boldsymbol{x}, \tag{1.1}$$

where $c_m = c_m(\boldsymbol{x},t)$, $m = 1,\cdots,M$, is the concentration of the m-th ionic species where $\boldsymbol{x} \in \Omega \subset \mathbb{R}^d$ indicates the location and $t > 0$ indicates the time [7]. The first part of the right hand of (1.1) is the entropy term which describes the particle Brownian motion of the ions. And the second part $\phi_{\rm ES}(\cdot)$ is the electrostatic potential where the electric field is created by the charge on different ionic species in most cases we considered. In addition, we focus on the steric repulsion arising from the finite size of solid ions [2, 9, 15, 21], which is the last term of (1.1). Here all physical parameters are set as 1 for simplicity in representation. Furthermore, additional free energy due to physical effects such as screening [6] can also be included in (1.1), which leads to different field equations. The field equations might either be defined on the whole domain $\mathbb{R}^n$ or a bounded domain Ω equipped with certain physical boundary conditions. However, proposing an appropriate boundary condition is a task of great difficulty as well as an interesting research subject. In this paper, we consider only the unbounded domain $\mathbb{R}^n$ and focus on the generalised field model. We remark that, there have been other ways of modeling ionic and water flows when considering voids, polarization of water, and ion-ion and ion-water correlations [18, 19].

The chemical potential ψ_m of the m-th ionic species is described by the variational derivative

$$\psi_m = \frac{\delta \mathcal{F}(c_m(\cdot,t))}{\delta c_m} \tag{1.2}$$

and is referred to in channel biology as the "driving force" for the current of the m-th ionic species [7]. Then EnVarA gives us both the equilibrium and the non-equilibrium (time dependent) equations for complex ionic fluids as follows,

$$\text{equilibrium:} \quad 0 = \nabla \cdot (c_m \nabla \psi_m), \quad m = 1,\cdots,M, \tag{1.3}$$

$$\text{non-equilibrium (time dependent):} \quad \partial_t c_m = \nabla \cdot (c_m \nabla \psi_m), \quad m = 1,\cdots,M. \tag{1.4}$$

In this paper, we consider the steric repulsion in the following form

$$\psi_{\rm FSE}(\cdot) = \frac{1}{2}\theta(\boldsymbol{x})(\mathcal{W} * \theta)(\boldsymbol{x}),$$

where the total density $\theta(\boldsymbol{x}) := \sum_{m=1}^{M} c_m$ and the electrostatic potential

$$\phi_{\rm ES}(\cdot) = \frac{1}{2}\rho(\boldsymbol{x})(\mathcal{K} * \rho)(\boldsymbol{x}),$$