Fluctuating hydrodynamics for ionic liquids

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A B S T R A C T

We present a mean-field fluctuating hydrodynamics (FHD) method for studying the structural and transport properties of ionic liquids in bulk and near electrified surfaces. The free energy of the system consists of two competing terms: (1) a Landau–Lifshitz functional that models the spontaneous separation of the ionic groups, and (2) the standard mean-field electrostatic interaction between the ions in the liquid. The numerical approach used to solve the resulting FHD-Poisson equations is very efficient and models thermal fluctuations with remarkable accuracy. Such density fluctuations are sufficiently strong to excite the experimentally observed spontaneous formation of liquid nano-domains. Statistical analysis of our simulations provides quantitative information about the properties of ionic liquids, such as the mixing quality, stability, and the size of the nano-domains. Our model, thus, can be adequately parameterized by directly comparing our prediction with experimental measurements and all-atom simulations. Conclusively, this work can serve as a practical mathematical tool for testing various theories and designing more efficient mixtures of ionic liquids.

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1. Introduction

In the past decade, extensive studies have been conducted on room temperature ionic liquids (RTIL) mainly because of their intriguing physical properties as compared to the traditional electrolytes [1,2]. Their potential applications include high storage devices (super-capacitors) [3], batteries [4], lubrication of micro-electromechanical machines [1], dye-sensitized photoelectrochemical cells [5], and gating devices [2]. In a nutshell, RTIL can be considered as a new type of electrolyte due to their wide range of structural transitions near electrified surfaces [6,7]. Experimental studies and atomistic-level simulations have reported overscreened and crowded aggregations of ions near electrodes that are accompanied by lamellar, bicontinuous, and sponge-like layerings [8–12]. This structural morphology of RTIL can be tuned accordingly to increase the energy density and modify the transport properties of the electric double bilayer (EDL), i.e., the interface between the ionic liquid and a charged metallic surface [13].

Traditional mean-field studies for dilute electrolytes, such as the Gouy–Chapman–Stern (GCS) theory [14], predict the formation of an exponentially decaying charged layer near the metallic surface. Such behavior results in capacitance that is a monotonic function of the applied electric field. Recent experiments, however, have

revealed a voltage-driven anomalous differential capacitance resulting from sudden changes in liquid morphology at the EDL [15]. This behavior has signatures of first-order phase transition and calls for theoretical studies beyond the traditional GCS approach. Modified mean-field models are capable of capturing screened and crowded interfacial effect that results in a non-monotonic voltage dependence of the capacitance [16,2,17]. However, they do not predict a first-order phase transition. Very recently, Limmer introduced a novel mean-field model that describes the experimentally observed anomalous behavior of the capacitance [18]. He particularly showed that this phenomenon results from the interplay of the short-range repulsion and long-range electrostatic interactions between the oppositely charged ionic groups. Using a Landau–Lifshitz–Poisson model, Gavish and Yochelis proceeded one step further and studied the interplay between the bulk nano-domains and the periodic layering at EDL [19]. Lee and Perkin followed a substantially different approach and showed that ion–image interaction might explain the anomalous transition in the differential capacitance [20]. They also mentioned that this behavior depends on the bulk energy of the RTIL.

The above mentioned theoretical approaches have *qualitatively* explained the mechanisms underlying the intriguing morphology of RTIL. However, these methods cannot provide quantitative results that could help design more efficient ionic liquids mixtures. The problem is simply too complicated to be solved analytically near electrified surfaces. Besides, deterministic numerical simulations cannot provide reliable predictions since they do not probe

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the entire free energy landscape of the system. To overcome this limitation, we present a stochastic mathematical model that directly compares with the experimental observations and all-atom molecular dynamics simulations. Our approach describes thermal noise through the standard FHD framework, which is a relatively well-developed method for modeling nanoscale fluid dynamics. Although initially introduced in an attempt to describe thermal fluctuations in homogeneous liquids [21], FHD has now become sophisticated enough to model mass, momentum, and energy transfer [22–29] in multiphase–multicomponent fluid flows [30,31] with or without reactive species [32,33] for length scales as small scales as 5 Å [24]. FHD has also been incorporated in many popular fluid–structure methods to capture the effect of fluid thermal fluctuations on nanostructure dynamics [34–39,24].

In this study, we present an FHD approach for ionic liquids designed to model not only the morphology but also the transport properties of the mixture. For this purpose, the governing equations of the system include the mass, component, and momentum balance equations coupled with the Poisson equation that provides the electrostatic potential in the system. To describe the spontaneous component separation, we consider a Landau–Lifshitz free energy functional similar to the Ref. [19] but appropriately modified to accommodate thermal fluctuations. The spatial gradients are approximated using the central difference staggered scheme presented in Ref. [24], while the time integration of the governing equations is performed using a stochastic second order Runge–Kutta method [42]. The Poisson equation is solved simultaneously at each time step using a fast Fourier transform (FFT). Extensive numerical simulations proved that our approach can accurately reproduce the statistical fluctuations of the density fields and describe the experimentally observed nanostructuring in the bulk and near the EDL. We also show that the presence of thermal fluctuations may lead the system to ground states that are substantially different compared to the steady states of deterministic simulations of ionic liquids. Our approach, thus, can provide a quantitative analysis of RTIL and be a numerical framework for testing various theories and designing more efficient ionic liquids mixtures at the nanoscale.

The structure of the paper is as follows. In Sec. 2, we introduce the FHD equations for ionic liquids, and in Sec. 3, we present the numerical scheme used to solve the stochastic partial differential equations. In Sec. 4, we present the results of our numerical simulations. Specifically, Sec. 4.1 is devoted to the dynamics of RTIL in the absence of an external electrostatic field. We first validate the accuracy of our numerical approach and then statistically analyze the fluctuations of the order parameters. In Sec. 4.2, we model an ionic liquid nanoconfined between two oppositely charged electrodes (nano-capacitor) and discuss the ability of our approach to reproduce the intriguing morphology of ionic liquids. Differences between stochastic and deterministic modeling of ionic liquids are also discussed. Finally, in Sec. 5, we briefly summarize and discuss our results.

2. FHD equations for ionic liquids

We have assumed a symmetric ionic liquid that consists of monovalent anions and cations of charge per unit mass $z_+ = z_0$ and $z_- = -z_0$, respectively, where $z_0 \in \mathbb{R}^+$. If ρ_+ and ρ_- represent the mass density of the two opposite ions, we can define the total mass density of the system as $\rho = \rho_+ + \rho_-$ and the mass fraction difference as $c = c_+ - c_-$, where $c_+ = \rho_+/\rho$ and $c_- = \rho_-/\rho$. The total charge per mass unit is given by $z = z_0 \rho c$. If the electrostatic potential of the system is denoted by ϕ, and $\mathbf{x} \in \mathbb{R}^3$ represents the spatial coordinates, the total mean field energy of the system can be written as

$$F = F_0[c(\mathbf{x}), \rho(\mathbf{x})] + F_e[c(\mathbf{x}), \rho(\mathbf{x}), \phi(\mathbf{x})]. \tag{1}$$

The first term in Eq. (1) represents the free energy of the system in the absence of electrostatic interaction and is given by a Ginzburg–Landau functional

$$F_0[c(\mathbf{x}), \rho(\mathbf{x})] = \int \left(\psi_c(c) + \frac{k_c}{2}|\nabla c|^2 + \psi_\rho(\rho) + \frac{k_\rho}{2}|\nabla \rho|^2 \right) d\mathbf{x}, \tag{2}$$

where ψ_ρ and ψ_c are the local free energy densities for the order parameters and ρ and c, respectively. Both local terms have a double well structure, i.e., $\psi_\rho(\rho) = A(\rho - \rho_l)^2(\rho + \rho_v)^2$, with minima at ρ_l (liquid) and ρ_v (vapor), and $\psi_c(c) = B(c-1)^2(c+1)^2/2$ with two minima at -1 (cations) and $+1$ (anions). The coefficients A and B are a measure of the barrier heights. The mass density and mass fraction square gradients represent the free energy penalty for having phase and component interfaces, respectively, where k_ρ and k_c are the corresponding gradient coefficients.

The second term in Eq. (1) is the electrostatic energy of the system

$$F_e[c(\mathbf{x}), \rho(\mathbf{x}), \phi(\mathbf{x})] = \int \left(z_0 \rho c \phi - \frac{1}{2}\epsilon |\nabla \phi|^2 \right) d\mathbf{x}, \tag{3}$$

where ϵ is the permittivity.

Under these assumptions, the mass, momentum and component balance equations are written as follows:

$$\frac{\partial \rho}{\partial t} = -\nabla \cdot \mathbf{g}, \tag{4}$$

$$\frac{\partial \mathbf{g}}{\partial t} = \nabla \cdot (\mathbf{R} + \mathbf{\Pi} + \widetilde{\mathbf{\Pi}}), \tag{5}$$

$$\frac{\partial(\rho c)}{\partial t} + \nabla \cdot (\rho c \boldsymbol{v}) = -\nabla \cdot (\mathbf{J} + \widetilde{\mathbf{J}}), \tag{6}$$

$$\nabla^2 \phi = \frac{z \rho c}{\epsilon}, \tag{7}$$

where $t \in \mathbb{R}^+$, $\mathbf{g} = \rho \boldsymbol{v}$ is the momentum density, and $\boldsymbol{v}$ the velocity field of the fluid. The three tensors, $\mathbf{R}$, $\mathbf{\Pi}$ and $\widetilde{\mathbf{\Pi}}$, in the momentum balance equation (Eq. (5)), are the reversible, viscous, and fluctuating stress, respectively. Deriving the momentum balance equation through the least action principle shows that $\nabla \cdot \mathbf{R} = -\rho \nabla(\delta F/\delta \rho)_c + (\delta F/\delta c)_\rho \nabla c$, which leads to

$$\nabla \cdot \mathbf{R} = \nabla \cdot \mathbf{R}^\rho + \nabla \cdot \mathbf{R}^c - z_0 \rho c \nabla \phi, \tag{8}$$

where

$$\mathbf{R}^\rho = \left[-p_0 - k_\rho \rho \nabla^2 \rho + \frac{k_\rho |\nabla \rho|^2}{2} \right] \mathbf{I} - k_\rho \nabla \rho \otimes \nabla \rho \tag{9}$$

and

$$\mathbf{R}^c = \left[\psi_c(c) + \frac{k_c}{2}|\nabla c|^2 \right] \mathbf{I} - k_c \nabla c \otimes \nabla c \tag{10}$$

are the reversible stress tensors for the order parameters ρ and c, respectively. In this work, we have assumed that there is no liquid–vapor phase separation and have neglected the mass density gradient. In Eq. (9), p_0 is the thermodynamics pressure, i.e., $p_0 = \rho \partial \psi_\rho / \partial \rho - \psi_\rho$ [30]. For simplicity, we have assumed that $\mathbf{R}_\rho$ is the hydrodynamic pressure of the system

$$\mathbf{R}^\rho \simeq c_T^2 \rho \mathbf{I}, \tag{11}$$

where c_T is the sound velocity of the mixture. We also have assumed that the velocity fluctuations are small enough to neglected the nonlinear advection term in Eq. (5). The Newtonian dissipative stress in momentum balance equation is expressed as