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Efficiently accounting for ion correlations in electrokinetic nanofluidic devices using density functional theory

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ABSTRACT

The electrokinetic behavior of nanofluidic devices is dominated by the electrical double layers at the device walls. Therefore, accurate, predictive models of double layers are essential for device design and optimization. In this paper, we demonstrate that density functional theory (DFT) of electrolytes is an accurate and computationally efficient method for computing finite ion size effects and the resulting ion–ion correlations that are neglected in classical double layer theories such as Poisson–Boltzmann. Because DFT is derived from liquid-theory thermodynamic principles, it is ideal for nanofluidic systems with small spatial dimensions, high surface charge densities, high ion concentrations, and/or large ions. Ion–ion correlations are expected to be important in these regimes, leading to nonlinear phenomena such as charge inversion, wherein more counterions adsorb at the wall than is necessary to neutralize its surface charge, leading to a second layer of co-ions. We show that DFT, unlike other theories that do not include ion–ion correlations, can predict charge inversion and other nonlinear phenomena that lead to qualitatively different current densities and ion velocities for both pressure-driven and electro-osmotic flows. We therefore propose that DFT can be a valuable modeling and design tool for nanofluidic devices as they become smaller and more highly charged.

1. Introduction

Fluidic devices fabricated with nanometer-scale features hold the promise to analyze, separate, concentrate, manipulate, and detect specific molecules with exquisite sensitivity and high throughput. Applications include DNA sequencing, medical testing, and biowarfare defense [1]. These applications can be realized because the fluids are confined to slits or channels whose smallest dimension is tens of nanometers in size (with the other dimensions still macroscopic). The smaller the confining direction is, the more that surface effects—which are negligible in macroscopic systems—come to dominate over normal bulk properties. The ionic current and velocities through these nanoscale electrokinetic devices is then defined by the structure of the electrical double layers at the device walls.

The interactions at the solid/liquid interface can occur via several mechanisms [2]. Even in the absence of chemical bonding between any of the molecules, there are steric and electrostatic interactions between the fluid and the wall molecules. In many contemporary nanofluidic devices, the surface charge of the channel walls is large enough that the nonlinear coupling between these "simple" interactions gives the device novel properties that change with ion type and concentration [3,4]. Therefore, one of the first goals toward the development of truly unique nanofluidic devices is a robust theory of the solid/liquid interface to predict—even if just qualitatively—device behavior with different electrolytes, electrolyte concentrations, flow conditions, and nanochannel surfaces.

To model the solid/liquid interface of an electrolyte in a nanofluidic channel, ideally one would use all-atom molecular simulations. While they have provided useful insights, these models remain too computationally expensive to be relevant at the time and length scales of dynamic nanofluidic phenomena [5]. Unfortunately, theories that span these scales necessarily trade computation time for less accurate representations of ion–ion and ion–wall interactions. As recently reviewed by Bazant et al. [6], several models have been proposed to extend the classic Gouy–Chapman–Stern theory for dilute solutions [7–9] to include steric effects due to the finite size of ions.

Perhaps the simplest such model was developed by Bikerman [10], wherein the accumulation of ions is limited by capping each ion's packing fraction. Bikerman's model has garnered renewed interest in recent years (see Bazant et al. [6] for references), and, despite its simplicity, yields predictions that are qualitatively different from the Gouy–Chapman–Stern theory. For example,

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Bikerman's model yields a differential capacitance that decreases with voltage [11], as opposed to the exponential growth in Gouy–Chapman–Stern theory. It also predicts the experimentally observed flow-reversal at high frequencies in AC electro-osmosis [12]. Other, more sophisticated, models to account for ion size incorporate the Boublik–Mansoori–Carnahan–Starling–Leland (BMCSL) equation of state for a hard-sphere liquid [13–15]. However, as we will show, these kinds of models cannot account for ion–ion correlations that occur in nanofluidic systems under a wide range of experimental conditions.

In this paper, we use density functional theory (DFT) of fluids [16–19], a theory that aims to fill the gap between computational efficiency and thermodynamic accuracy. DFT of fluids—not to be confused with quantum mechanical DFT of electron orbitals—is derived from well-established thermodynamics to take into account the effects of finite ion size. The resulting ionic correlations include not only steric correlations, but also—and usually more importantly—electrostatic correlations beyond the mean electrostatic potential that is used in Poisson–Boltzmann (PB), Bikerman, and BMCSL theories. DFT has been used to successfully model a wide variety of fluids (reviewed by Wu [20]), including simple fluids [21–23], the electrical double layer [18,24–27], and biological ion channels [28–31]. Nilsen and Griffiths [32] used DFT to study electrokinetics of monovalent ions in slits that were only several ion diameters wide. However, as yet DFT has not found widespread use in modeling nanofluidic phenomena, despite the fact that ion–ion correlations are expected to be important. The goal of this paper is to focus on situations where DFT describes experimental effects not captured in simpler theories.

In Section 2, we provide a brief description of DFT (including the basic equations to model a planar charged wall) and its general advantages and disadvantages compared with other, simpler theories. In Section 3, we compare DFT of a single electrical double layer with more traditional, PB and Bikerman, theories in conditions relevant to the experimental nanofluidician. Furthermore, we will focus on those cases where PB-like theories break down and it is especially crucial to use more sophisticated models like DFT. Finally, in Section 4, we discuss DFT calculations of ion transport in nanofluidic systems. We find that electro-osmotic and pressure-driven currents can be qualitatively different for the same device under conditions where the finite size of ions must be taken into account.

2. Theory

In this work, we consider a typical nanofluidic device with a single-slit geometry where ions move along the x-direction between $x = 0$ to $x = L$ and electrical double layers are created by charged slit walls at $y = 0$ and $y = H$. We assume that both the length L and the width W (in the z-direction) are macroscopic compared with the nanoscale dimension H and that ionic concentrations do not change in the x- and z-directions. Such a geometry is the most prevalent in experimental nanofluidic systems to date [1].

In this geometry, all three of the theories that we consider in this paper (PB, Bikerman, and DFT) can be described within the same mathematical framework. Specifically, in the y-direction, the ions are in equilibrium and the concentration profiles are computed from the ions' excess electrochemical potentials:

$$\rho_i(y) = \rho_i^{\text{bath}} \exp\left(-\frac{z_i e}{kT}\psi(y) - \Delta\mu_i^{\text{ex}}(y) - U_i(y)\right). \tag{1}$$

Here, ρ_i^{bath} is the concentration in the bath (far from the wall) of ion species i with valence z_i and $\mu_i^{\text{ex}}(y)$ is the excess chemical potential of species i, with the Δ indicating that the bath value has been subtracted off. The fundamental charge is e, the Boltzmann constant k, and the absolute temperature T. The mean electrostatic potential ψ is computed from the Poisson equation

$$-\varepsilon\varepsilon_0 \frac{d^2\psi}{dy^2}(y) = e\sum_i z_i\rho_i(y) + \sigma\delta(y), \tag{2}$$

where σ is the surface charge on the wall, δ is the Dirac delta function, ε_0 is the permittivity of vacuum, and ε is the relative dielectric coefficient, which in this paper is assumed to be constant throughout the system. When we consider a single electrical double layer, the boundary conditions for Eq. (2) are that $d\psi(-\infty)/dx = 0$ and $\psi(\infty) = 0$. For a slit, $d\psi(\pm\infty)/dx = 0$. (In practice, $\pm\infty$ are taken to be finite large distances.) The last component is the function U_i, which defines where the centers of the ions can and cannot go:

$$U_i(y) = \begin{cases} 0 & \text{if} \quad s_i < y < H - s_i \\ \infty & \text{otherwise,} \end{cases} \tag{3}$$

where s_i is the distance of closest approach of species i. This may be the width of the Stern layer or the simply the radius of the ion itself, as described below.

DFT, PB, and generalizations of PB share this basic mathematical framework of self-consistent mean electrostatic potential determining the ion concentration profile. The models differ in the definition of the excess chemical potential, which in DFT plays an equal or greater role than $\psi(y)$. We will describe how DFT defines $\mu_i^{\text{ex}}(y)$ in the next section. In the remainder of this section, we describe two commonly used models that we will also use in this paper. In the notation of Eqs. (1)–(3), these are:

1. *PB* where $\Delta\mu_i^{\text{ex}}(y) = 0$ and $s_i = 0$ except in one case of very large ions (shown later in Fig. 3) where $s_i = R_i$, the radius of ion species i.
2. *Bikerman* where $s_i = 0$ and

$$\mu_i^{\text{ex}}(y) = -kT\ln\left(1 - 8\sum_j R_j^3\rho_j(y)\right). \tag{4}$$

We note that the different distances of closest approach s_i of the ions (the radius in DFT and zero in the PB and Bikerman models) complicates direct comparisons of ion profiles near the wall. Such complications must be handled for very precise comparisons. However, the purpose of our comparing DFT to these models is only to illustrate the *qualitative* differences between generalized PB models and DFT for phenomena like charge inversion and ion packing and to illustrate approximately under what conditions such phenomena start to occur in DFT.

2.1. DFT of charged, hard spheres

We consider the primitive model of ions where ions are charged, hard spheres with the same dielectric constant as the solvent. The primitive model has been useful in understanding the electrical double layer [33,34]. It is also the simplest model to reproduce much experimental data, including activity coefficients [35], ionic currents through biological ion channels [29], and synthetic nanopores [4]. Later in this paper, we will also use the primitive model to reproduce experimental nanofluidics data.

For bulk electrolytes (i.e., when ion concentrations are homogeneous), there are several theories for modeling the excess chemical potential of primitive model ions, including the Debye/Hückel, mean spherical approximation (MSA), and hypernetted chain theories, to name only a few (review by Barthel et al. [36]). When the ion distributions are inhomogeneous (e.g., near a wall), the excess chemical potential and ion concentration profiles can be computed with integral equations and DFT. Integral equation theory (reviewed by Hansen and McDonald [37]), like DFT, includes the